Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Unique thermodynamic relationships for $\Delta_f H^o$ and $\Delta_f G^o$ for crystalline inorganic salts. I. Predicting the possible existence and synthesis of Na_2SO_2 and Na_2SeO_2

Ángel Vegas,[a,b] Joel F. Liebman[c] and H. Donald Brooke Jenkins[d]*

[a]Universidad de Burgos, Parque Científico y Tecnológico, Edificio I+D+I, Plaza Misael Bañuelos, Burgos 09001, Spain, [b]Instituto de Química Física 'Rocasolano', CSIC, Madrid, Spain, [c]Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Maryland 21250, USA, and [d]Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, England

Correspondence e-mail: h.d.b.jenkins@warwick.ac.uk

Received 21 May 2012
Accepted 5 July 2012

The concept that equates oxidation and pressure has been successfully utilized in explaining the structural changes observed in the M_2S subnets of M_2SO_x (x = 3, 4) compounds (M = Na, K) when compared with the structures (room- and high-pressure phases) of their parent M_2S 'alloy' [Martínez-Cruz *et al.* (1994), *J. Solid State Chem.* **110**, 397–398; Vegas (2000), *Crystallogr. Rev.* **7**, 189–286; Vegas *et al.* (2002), *Solid State Sci.* **4**, 1077–1081]. These structural changes suggest that if M_2SO_2 would exist, its cation array might well have an *anti*-CaF_2 structure. On the other hand, in an analysis of the existing thermodynamic data for M_2S, M_2SO_3 and M_2SO_4 we have identified, and report, a series of unique linear relationships between the known $\Delta_f H^o$ and $\Delta_f G^o$ values of the alkali metal (M) sulfide (x = 0) and their oxyanion salts M_2SO_x (x = 3 and 4), and the similarly between M_2S_2 disulfide (x = 0) and disulfur oxyanion salts $M_2S_2O_x$ (x = 3, 4, 5, 6 and 7) and the number of O atoms in their anions x. These linear relationships appear to be unique to sulfur compounds and their inherent simplicity permits us to interpolate thermochemical data ($\Delta_f H_o$) for as yet unprepared compounds, M_2SO (x = 1) and M_2SO_2 (x = 2). The excellent linearity indicates the reliability of the interpolated data. Making use of the volume-based thermodynamics, VBT [Jenkins *et al.* (1999), *Inorg. Chem.* **38**, 3609–3620], the values of the absolute entropies were estimated and from them, the standard $\Delta_f S^o$ values, and then the $\Delta_f G^o$ values of the salts. A tentative proposal is made for the synthesis of Na_2SO_2 which involves bubbling SO_2 through a solution of sodium in liquid ammonia. For this attractive thermodynamic route, we estimate ΔG^o to be approximately -500 kJ mol^{-1}. However, examination of the stability of Na_2SO_2 raises doubts and Na_2SeO_2 emerges as a more attractive target material. Its synthesis is likely to be easier and it is stable to disproportionation into Na_2S and Na_2SeO_4. Like Na_2SO_2, this compound is predicted to have an anti-CaF_2 Na_2Se subnet.

1. Introduction

Emerging in recent studies (see for example, Nalbandyan & Novikova, 2012), is the usefulness of combining simple thermodynamic ideas (obtained by using volume-based thermodynamics, VBT) with structural science concepts in order to gain new insights into the structural characteristics of condensed phases.

This present article bridges the topics of energetics (thermodynamics) and structural science, often using the VBT approach in order to obtain the thermodynamics. This latter procedure requires no structural details whatsoever (Glasser & Jenkins, 2011*a*) and relies only on knowing the *volume* of the formula unit involved. However, once combined with

Vegas' oxygen–pressure concept (Martínez-Cruz *et al.*, 1994) this enables the capability of VBT to be extended and structural details also can then emerge.

In 1994 Vegas and co-workers pointed out the equivalence between oxidation and pressure (Martínez-Cruz *et al.*, 1994). That is to say that adding O atoms to a lattice during oxidation creates an internal pressure within the lattice. This idea was based on high-pressure (HP) experiments carried out by Beck & Lederer (1993) on the BaSn alloy which at 3.5 GPa underwent the *B*33 → CsCl transition. It is well known that cations in perovskites, like $BaSnO_3$ ($Pm\bar{3}$), are also CsCl-type, so that both HP-BaSn and $BaSnO_3$ have a common pattern. The important issue of this coincidence was that their similarity was not only topological but that their unit-cell dimensions were almost equal (4.07 and 4.11 Å for BaSn and $BaSnO_3$). Thus, the evidence was that the insertion of three O atoms into the *B*33 network of BaSn produced the same effect as the application of a pressure of 3.5 GPa.

This concept which equates oxidation with the resultant imposed internal pressure (caused by *stuffing* the O atoms into the lattice) has been successfully utilized in order to explain – in qualitative terms – the structural changes observed in the cation substructures of many oxides when compared with the structure of their parent 'alloy' (Martínez-Cruz *et al.*, 1994; Vegas, 2000; Vegas & Jansen, 2002). Among them, the system Na_2S/Na_2SO_x has received special attention with high-pressure experiments being performed on Na_2S (Vegas *et al.*, 2001) and with attendant crystal chemical studies of both the Na_2S phases and their corresponding existing oxides Na_2SO_3 and Na_2SO_4 (Vegas & García-Baonza, 2007; Vegas, 2011). Such studies showed the existence of a direct relationship between the Na_2S substructures and the oxygen contents of the Na_2SO_X oxide, as well as discussing the opposing role (to pressure) of temperature (where we see expansion of the lattice) in determining the observed phase transitions. In the case of Na_2S, high-pressure experiments showed the double transition CaF_2 → $PbCl_2$ → Ni_2In (Vegas *et al.*, 2001). A further paper dealing with theoretical calculations on $K/K_2S/K_2SO_4$ has been published by Vegas & Mattesini (2010). However, a comprehensive study including many alkali sulfates and selenates (Vegas, 2011) suggests that the M_2S sulfides would follow the transition path 1 as a result of successively increasing the *external* pressure.

CaF_2 → Ni_2Al → $PbCl_2$ → Ni_2In → $TiSi_2$ → $MgCu_2$

Path 1

Several of these binary phases correspond to one of the observed Na_2S substructures found within the known phases of Na_2SO_3 and Na_2SO_4. Thus, in Na_2SO_3 the Na_2S substructure is of the Ni_2Al type, whereas in V-Na_2SO_4 (thenardite), it has a $TiSi_2$-type subarray at room temperature, transforming at high temperature into the I-Na_2SO_4 phase, with a Na_2S subarray of the hexagonal Ni_2In-type. The $PbCl_2$ structure is not found in any Na_2SO_4 phase, but it *is* present in the room-temperature phase of the related K_2SO_4. Thus, in this way, a higher O content stabilizes those phases which correspond to higher-pressure phases. Within this scheme has been suggested the possible existence of Na_2SO_2 sulfoxylate, whose lower O content, in terms of the 'oxidation–pressure' concept, should yield a structure closer to the room-pressure phase of Na_2S (*i.e.* the *anti*-CaF_2-type structure of the parent Na_2S). The structure proposed for Na_2SO_2 is represented in Fig. 1. An analogous situation is anticipated for Na_2SeO_2, which should be much easier to synthesize.

Historically, one of us (ÁV) proposed the synthesis of Na_2SO_2 to Martin Jansen, during a stay in Stuttgart in 2000. Jansen has reported to us that the synthesis was attempted, under his direction, by a Diploma student (Wiench, 1975) who

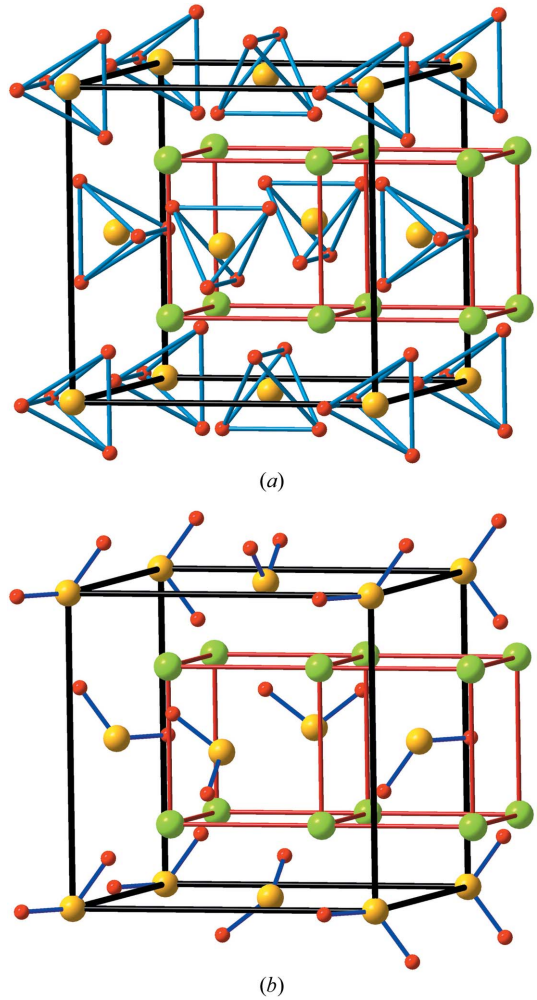

Figure 1
Two perspective views of hypothetical Na_2SO_2 or the Na_2SeO_2 structures. (*a*) An *anti*-CaF_2 structure formed by 2 Na atoms (green) and SO_4 (or SeO_4 tetrahedra) (S: yellow; O: red). The $S(Se)O_2$ groups are represented as tetrahedral to indicate that the O atoms cannot be located. The SO_4 tetrahedra should be taken as disordered SO_2 groups. (*b*) The same *anti*-CaF_2-type structure of Na_2SO_2 or Na_2SeO_2 showing the simple cubic array of the Na atoms (green) alternately filled by the SO_2 (or SeO_2) groups (S: yellow; O: red). In turn, the S atoms (yellow) form a f.c.c. array where all the tetrahedra are filled by the Na atoms. In this case, two O atoms from the tetrahedra drawn in (*a*) have been deleted randomly to form the SO_2 (or SeO_2) groups. Their random orientation indicates that their positions are unpredictable and that in the cubic CaF_2-type structure ($Fm\bar{3}m$) they must necessarily show positional disorder.

Table 1
Equations of best fit for data in Table 2 using data from Wagman *et al.* (1982).

Column 6 lists the values of x for which experimental values (in Table 2) are available. In order to assess the errors in predicted values we can calculate the predicted experimental values = $Kx + C$ and compare these with the experimentally known value. (Predicted − experimental) is the magnitude of the error in each of the values. We then quote the square root of the sum of the squares of these errors in the $x = 0$ and $x = 3$ values in column 8. This then approximates the errors caused by interpolation for $x = 1$ and $x = 2$ for M_2SO_x salts. In the case of $M_2S_2O_x$ salts the overall r.m.s. error is quoted in column 8. This may overestimate the interpolation errors in most of these cases.

Item number	M	K [kJ mol^{-1} (O atom)$^{-1}$]	C (kJ mol^{-1})	Correlation coefficient, R^2	No. of points, N, x values	Error (kJ mol^{-1})†	Average errors on interpolation of values (kJ mol^{-1})‡
Sulfoxylates							
1	$\Delta_fH^o(Li_2SO_x,c)$	−248.0	−439.8	0.999	3 x = 0, 3, 4	x = 0; −1.6 (0.4%) x = 3; 6.8 (0.6%) x = 4; −4.7 (0.3%)	± 3.5
2	$\Delta_fH^o(Na_2SO_x,c)$	−253.2	−360.1	0.999	3 x = 0, 3, 4	x = 0; −4.7 (1.3%) x = 3; 18.9 (1.7%) x = 4; −14.2 (1.0%)	± 9.3
3	$\Delta_fG^o(Na_2SO_x,c)$	−228.0	−345.6	0.999	3 x = 0, 3, 4	x = 0; −4.2 (1.2%) x = 3; 17.1 (1.7%) x = 4; −12.6 (1.0%)	± 8.8
4	$\Delta_fH^o(Na_2S_2O_x,c)$	−215.1	−413.0	0.996	6 x = 0, 3, 4, 5, 6, 7	x = 0; 15.9 (4.0%) x = 3; −64.7 (5.8%) x = 4; 41.2 (3.3%) x = 5; 10.3 (0.7%) x = 6; 4.6 (0.3%) x = 7; −6.4 (0.3%)	± 11.1
5	$\Delta_fG^o(Na_2S_2O_x,c)$	−189.6	−406.9	0.997	4 x = 0, 3, 6, 7	x = 0; 28.2 (7.4%) x = 3; −52.3 (5.1%) x = 6; 12.5 (0.8%) x = 7; 11.8 (0.7%)	± 14.9
6	$\Delta_fH^o(K_2SO_x,c)$	−260.6	−373.3	0.998	3 x = 0, 3, 4	x = 0; −7.4 (1.9%) x = 3; 29.6 (2.6%) x = 4; −22.2 (1.5%)	± 10.1
7	$\Delta_fG^o(K_2SO_x,c)$	−239.1	−374.5	0.991	3 x = 0, 3, 4	x = 0; −10.5 (2.9%) x = 3; 53.8 (5.2%) x = 0; −9.5, (0.7%)	± 18.2
8	$\Delta_fH^o(K_2S_2O_x,c)$	−218.4	−459.2	0.997	5 x = 0, 3, 5, 6, 7	x = 0; 27.0 (6.2%) x = 3; −59.3 (5.0%) x = 5; 17.2 (1.1%) x = 6; 13.9 (0.8%) x = 7; 1.2 (0.1%)	± 13.0
9	$\Delta_fH^o(Rb_2SO_x,c)$	−268.7	−360.7	1.000	2 x = 0, 4	Only two points available	No error estimable
10	$\Delta_fH^o(Cs_2SO_x,c)$	−267.9	−354.2	0.999	3 x = 0, 3, 4	x = 0; 5.8 (1.6%) x = 3; 23.2 (2.0%) x = 4; 17.2 (1.2%)	± 8.0
Sodium selenoxylates							
11	$\Delta_fH^o(Na_2SeO_x,c)$	$23.8x^2 - 277.2\,x - 341.4$§		1.00	3 x = 0, 3, 4	Only two points available	No error estimable

† Error = e_x = (predicted − actual) (kJ mol^{-1}) and percentage error of prediction (%) for the cases (x) in which the experimental value is known. ‡ Average errors on interpolation of values (kJ mol^{-1}), *e.g.* between $x = 0$ and $x = 3$, error is $\frac{1}{2}(e_0^2 + e_3^2)$. In general they are: $(1/n)(\Sigma^n_{i=0}e_i^2)$. § NB Not being a sulfur compound, a linear relationship needs to be replaced by a polynomial curve of degree 2 (quadratic) to form the basis of the fit for $\Delta_fH^o(Na_2SeO_x,c)$ *versus* x.

tried to obtain the compound by *heating* disodium peroxide with sulfur, in a sealed ampoule under vacuum. This synthesis route was unsuccessful and ÁV considered that a possible reason for the failure to synthesize the material was because of the high-temperature conditions employed. So in this present article new synthetic routes at lower temperature are explored making use of the magnitudes derived from the Jenkins VBT approach (Jenkins *et al.*, 1999; Jenkins, 2009; Glasser & Jenkins, 2011*b*).

The stages required towards examining the feasibility of the syntheses of sulfoxylates (and later disodium selenoxylate) are first to identify a suitable synthetic route from both a practical and a thermodynamic standpoint, and then to check on its thermodynamic stability in respect of proneness to decompose or disproportionate. The VBT theory (Jenkins *et al.*, 1999; Jenkins, 2009; Glasser & Jenkins, 2011*b*) appears to be the appropriate tool to determine the stability of these compounds in terms of their Δ_fH^o and Δ_fG^o magnitudes. The study will be extended to the whole family of oxysalts of the formulae M_2SO_X (x = 1–4) and $M_2S_2O_X$ (x = 3–7). Disodium selenoxylate, Na_2SeO_2, is given particular consideration.

Although likely synthesizable, the stability of disodium sulfoxylate, Na_2SO_2, cannot be *unequivocally* established. The stability of the dicaesium, Cs_2SO_2, and potassium salt, K_2SO_2,

Table 2
Standard thermochemical data for the salts, M_2SO_x and $M_2S_2O_x$ and M_2SeO_x in their crystalline (c) phases.

Literature (upright type): thermodynamic data (taken from Wagman *et al.*, 1982, unless otherwise specified) and (*in italics*) predicted data from this study. Errors in this table are taken to be the r.m.s. of the sum of the errors found for the known materials, *e.g.* error (kJ mol^{-1}) found for Δ_fH^o predicted for interpolated Li_2SO and Li_2SO_2 taken as ±3.5 (from item 1, column 8, Table 1).

Compound	Δ_fH^o (kJ mol^{-1})	Δ_fG^o (kJ mol^{-1})	S^o_{298} (J K^{-1} mol^{-1})
Sulfoxylates			
Li_2S	−441.4	–439.084[a]†	63.6[b]
			78 ± 15[c]‡
Li_2S_2	−438.1	–	–
Li_2SO	*−688 ± 7*[c]§	*−658 ± 11*[c]¶	*90 ± 15*[c]‡
Li_2SO_2	*−936 ± 7*[c]§	*−878 ± 11*[c]¶	*102 ± 15*[c]‡
Li_2SO_3	−1177.0	*−1092 ± 4*[c]¶	*114 ± 15*[c]‡
Li_2SO_4	−1436.49	−1321.77	115.1
	−1436.489[a]	−1321.58[a]	
Na_2S	−364.8	−349.8	83.7
		−354.551[a]	97 ± 2[d]
			109 ± 15[c]
Na_2S_2	−397.1	−378.7	105
Na_2SO	*−613 ± 19*[c]§	*−574 ± 18*[c]§	*115 ± 15*[c]
Na_2SO_2	*−867 ± 24*[c]§	*−802 ± 22*[c]§	*121 ± 15*[c]
Na_2SO_3	−1100.8	−1012.5	145.94
	−1096.78 ± 0.81[e]	−1012.326[a]	*124 ± 15*[c]
	−1101.8 ± 0.7[f]		
	−1100.802[a]		
Na_2SO_4	−1387.1	−1270.2	149.6
	−1387.816[a]	−1269.848[a]	*136 ± 15*[c]
Na_2S_2O	*−628 ± 79*[c]§	*–597 ± 62*[c]§	–
$Na_2S_2O_2$	*−843 ± 79*§	*–786 ± 62*§	–
$Na_2S_2O_3$	−1123.0	−1028.0	155
$Na_2S_2O_4$	−1232.2	–	–
$Na_2S_2O_5$	−1478.2	*−1354 ± 62*[c]§	–
$Na_2S_2O_6$	−1699.04	−1531.8[g]	–
$Na_2S_2O_7$	−1925.1	−1722.1	202.1
K_2S	−380.7	−364.0	104.6
		−362.745[a]	*124 ± 15*[c]
K_2S_2	−432.2	–	–
K_2SO	*−634 ± 31*[c]§	*−613 ± 55*[c]§	*154 ± 15*[c]
K_2SO_2	*−895 ± 31*[c]§	*−853 ± 55*[c]§	*156 ± 15*[c]
K_2SO_3	−1125.5	−1038.030[a]§	*159 ± 15*[c]
	−1123.37 ± 0.96[e]		
K_2SO_4	−1437.79	−1321.43	175.6
		−1319.684[a]	*159 ± 15*[c]
K_2S_2O	*−678 ± 69*[c]§	–	–
$K_2S_2O_2$	*−896 ± 69*[c]§	–	–
$K_2S_2O_3$	−1173.6	–	–
$K_2S_2O_4$	*−1333 ± 69*[c]§	–	–
$K_2S_2O_5$	−1533.9	–	–
$K_2S_2O_6$	−1755.61	–	–
$K_2S_2O_7$	−1986.6	−1791.6	255
$K_2S_2O_8$	−1916.1	−1697.41	278.7
	−2182 ± 69[c]	–	–
Rb_2S	−360.7	*−350 ± 9*[c]†	*167 ± 15*[c] ‡
			133.9[b]
			150 ± 15 average
Rb_2SO	*−629*[c]§	*−594 ± 4*[c]¶	*171 ± 15*[c]‡
Rb_2SO_2	*−898*[c]§	*−833 ± 4*[c]¶	*174 ± 15*[c]‡
Rb_2SO_3	−1167[c]§	*−1073± 4*[c]¶	*177 ± 15*[c]‡
Rb_2SO_4	−1435.6	−1317.0	197.4
	−1435.07 ± 0.60[h]	−1316.91 ± 0.59[h]	199.60 ± 2.88[h]
		−1316.806[a]§	
Cs_2S	−360.0	*−348 ± 9*[c]†	*178 ± 15*[c]‡
			148.1[b]
			163 ± 30 average
Cs_2SO	*−622 ± 24*[c]§	*−587 ± 25*[c]¶	*185 ± 15*[c]‡
Cs_2SO_2	*−890 ± 24*[c]§	*–826 ± 25*[c]¶	*193 ± 15*[c]‡
Cs_2SO_3	−1134.7	*−1042± 4*[c]¶	*200 ± 15*[c]‡
Cs_2SO_4	−1443.0	−1323.7	211.9
		−1323.544[a]§	*200 ± 15*[c]‡
$Cs_2S_2O_5$	−1561.1	–	–

Table 2 (continued)

Compound	Δ_fH^o (kJ mol^{-1})	Δ_fG^o (kJ mol^{-1})	S^o_{298} (J K^{-1} mol^{-1})
Selenium compounds			
Na_2Se	−341.4	−339.9	129.8
			123 ± 15[c]‡
Na_2SeO_2	*−800.5*[c]§	*−738 ± 4*[c]¶	*131 ± 15*[c]‡
Na_2SeO_3	−958.6	*−865 ± 4*[c]¶	*129 ± 15*[c]‡
Na_2SeO_4	−1069.0	−941.7	117.7[g]
			148± 15[c]‡
SeO_2	−225.35[a]	−171.471[a]	66.693[a]

References: (*a*) Barin (1993); (*b*) Latimer (1961); (*c*) this work; (*d*) Lindberg *et al.* (2007); (*e*) O'Hare *et al.* (1986); (*f*) Cordfunke *et al.* (1987); (*g*) Karapet'yants & Karapet'yants (1970); (*h*) Palmer *et al.* (2002). † Indicates a Gibbs energy of formation value obtained by first estimating Δ_fS^o using the *averaged* standard absolute entropy estimate and then calculating $\Delta_fG^o = \Delta_fH^o - T\Delta_fS^o$. ‡ Indicates the standard absolute entropy value estimated using Jenkins & Glasser's (2003) equation: $S = kV_m + c$. § Indicates data obtained *via* least-squares fits in Table 1. ¶ Indicates a Gibbs energy of formation value obtained by first estimating Δ_fS^o using the standard absolute entropy estimate and then calculating $\Delta_fG^o = \Delta_fH^o - T\Delta_fS^o$.

however, seems established. Further we *can* predict, with much more certainty, the existence (stability) of disodium selenoxylate, Na_2SeO_2, and several suitably straightforward and thermodynamically favoured synthetic routes for this latter material.

2. Discussion

2.1. Trends in available thermodynamic data

In the normal run of things standard thermochemical data, Δ_fH^o and Δ_fG^o for a series of oxy salts, when plotted as a function of the number of O atoms present, x, will show an irregular variation. An example is shown in Fig. 2, where, for the series of sodium and potassium ox salts based on chlorine, $NaClO_x$ and $KClO_x$ ($0 \le x \le 4$), known standard enthalpy of formation data Δ_fH^o (Wagman *et al.*, 1982; Karapet'yants & Karapet'yants, 1970) when plotted *versus* x leads to irregular plots so making meaningful estimation of unknown intermediate values of Δ_fH^o, say for $x = 1$ for (NaClO) and $x = 1$ and 2 for K (KClO and $KClO_2$), virtually impossible. This

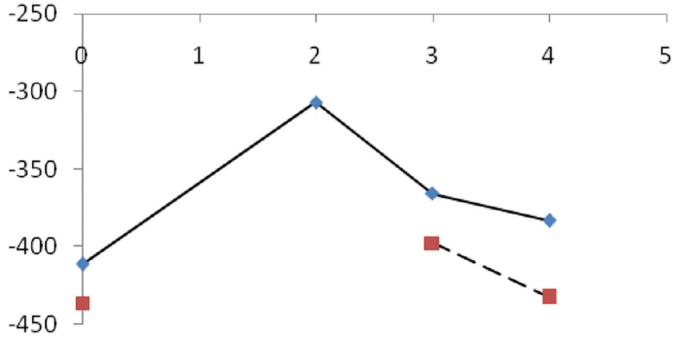

Figure 2
Plots of $\Delta_fH^o(NaClO_x,c)$/kJ mol^{-1} (x = 0, 2, 3, 4) (upper plot) and $\Delta_fH^o(KClO_x,c)$/kJ mol^{-1} (x = 0, 3, 4) (lower plot) as ordinate *versus* x as the abscissa, illustrating the *irregular* variation typically found with x for most oxysalts. The value for $\Delta_fH^o(KClO_2,c)$ is unknown. No values are recorded, of course, for (hypothetical) $\Delta_fH^o(NaClO,c)$ or $\Delta_fH^o(KClO,c)$.

situation, shown for chlorine oxy salts, is typical and is found in the case of oxy salts derived from almost every element in the periodic table.

In stark contrast, in the *unique* case of the element sulfur, a different scenario emerges. In the case of the oxy salts M_2SO_x and $M_2S_2O_x$ ($x < 8$), where M = alkali metal data (Wagman *et al.*, 1982; Karapet'yants & Karapet'yants, 1970; Barin, 1993), such as Δ_fH^o or Δ_fG^o as a function of x result in *linear* plots – possessing correlation coefficients each in excess of $R^2 = 0.990$. Plots can be made for $\Delta_fH^o(Li_2SO_x,c)$ ($x = 0, 3, 4$; Table 1, item 1), $\Delta_fH^o(Na_2SO_x,c)$ ($x = 0, 3, 4$; Table 1, item 2), $\Delta_fG^o(Na_2SO_x,c)$ ($x = 0, 3, 4$; Table 1, item 3), $\Delta_fH^o(Na_2S_2O_x,c)$ ($x = 0, 3$–7; Table 1, item 4), $\Delta_fG^o(Na_2S_2O_x,c)$ ($x = 0, 3, 6, 7$; Table 1, item 5), $\Delta_fH^o(K_2SO_x,c)$ ($x = 0, 3, 4$; Table 1, item 6), $\Delta_fG^o(K_2SO_x,c)$ ($x = 0, 4$; Table 1, item 7), $\Delta_fH^o(K_2S_2O_x,c)$ ($x = 0, 3, 5, 6$; Table 1, item 8), $\Delta_fH^o(Rb_2SO_x,c)$ ($x = 0, 4$; Table 1, item 9) and $\Delta_fH^o(Cs_2SO_x,c)$ ($x = 0, 3, 4$; Table 1, item 10). No plots can be made for $\Delta_fG^o(Li_2SO_x,c)$, $\Delta_fH^o(Li_2S_2O_x,c)$, $\Delta_fG^o(Li_2S_2O_x,c)$, $\Delta_fG^o(K_2S_2O_x,c)$, $\Delta_fG^o(Rb_2SO_x,c)$, $\Delta_fH^o(Rb_2S_2O_x,c)$, $\Delta_fG^o(Rb_2S_2O_x,c)$. In the plots for $\Delta_fG^o(K_2SO_x,c)(x = 0, 4$; Table 1 item 7) and $\Delta_fH^o(Rb_2SO_x,c)(x = 0, 4$; Table 1 item 9) only two data points are available and so linearity is assumed and therefore $R^2 = 1.00$. Errors are estimated from the agreement shown between known experimental data and the estimated data given by regression equations, the square root of the sums of the squares of the errors found for M_2S and for M_2SO_3 is used as an estimate for the error when interpolating values for M_2SO and M_2SO_2 (this is cited in Table 1, column 8). For the compounds $M_2S_2O_x$ an overall sum-of-squares error is quoted.

These observations make two things possible:

(i) It enables estimation of thermochemical data for well established salts merely by interpolation.

(ii) It also enables us to estimate data for hypothetical, and as yet unprepared compounds, examples being the thioperoxides, M_2SO ($x = 1$), and the sulfoxylates, M_2SO_2 ($x = 2$), since the data lie on (almost) perfect straight lines. This data can then be used to gain information on potential synthetic routes to these new materials.

Table 1 shows the rectilinear regression fits that can be made in cases where sufficient data exists in Table 2 to provide the listed plots. Table 2 lists all the known thermochemical data (Wagman *et al.*, 1982; Karapet'yants & Karapet'yants, 1970; Barin 1993) at 298 K and pressure 101 325 Pa for two separate families of alkali metal sulfur compounds, M_2SO_x and $M_2S_2O_x$. Table 2 summarizes the established experimental (upright type) and estimated (*italic* type) data assembled in this study.

Typical plots are illustrated in Fig. 3 for $\Delta_fH^o(Na_2SO_x,c)$ and $\Delta_fH^o(Na_2S_2O_x,c)$ *versus* x; in Fig. 4 for $\Delta_fH^o(K_2SO_x,c)$ and $\Delta_fH^o(K_2S_2O_x,c)$ *versus* x and in Fig. 5 for $\Delta_fG^o(Na_2SO_x,c)$ and $\Delta_fG^o(Na_2S_2O_x,c)$ *versus* x.

It is not possible to establish an analogous plot to Fig. 5 for K^+ salts simply because the majority of the data available in Wagman *et al.* (1982) is for aqueous salts (not the subject of this paper). It should be acknowledged that the only observed deviation from strict linearity occurs with the Δ_fH^o data ($x > 7$) for the salt $K_2S_2O_8$ which lies above (by 290 kJ mol^{-1}) the plot for the remaining salts containing less than eight O atoms. It is worthwhile noting, with respect to this compound, that the crystal structure determination is an old one, dating from 1935 and made using oscillating photographs. This data point has been *excluded* when fitting the analytical form for the data.

The existence of such simple plots makes the interpolation of missing data for these compounds straightforward with a high likelihood of being reasonably accurate.

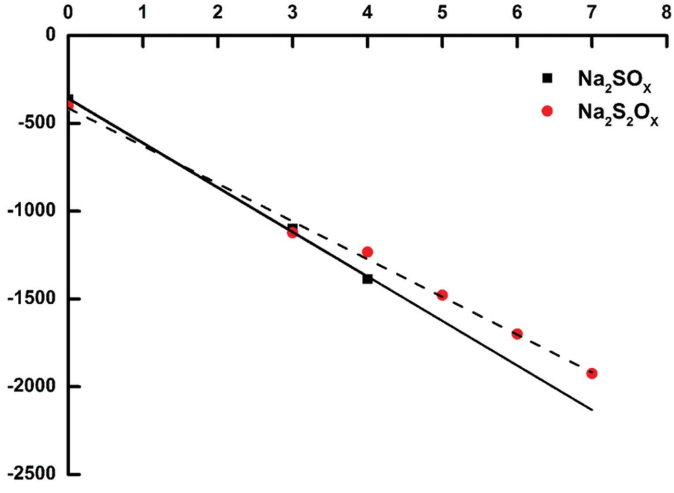

Figure 3
Plots of $\Delta_fH^o(Na_2S_2O_x,c)$/kJ mol^{-1} ($x = 0, 3, 4, 5, 6, 7$) as the ordinate *versus* x as the abscissa (dotted line), and $\Delta_fH^o(Na_2SO_x,c)$/kJ mol^{-1} ($x = 0, 3, 4$) as the ordinate *versus* x as the abscissa (solid line). Data from Table 2. Least-squares fitted lines take the forms: $\Delta_fH^o(Na_2S_2O_x,c)$/kJ mol^{-1} $\simeq -215.1x - 413.0$ for which $R^2 = 0.996$, $N = 6$ (item 4), $\Delta_fH^o(Na_2SO_x,c)$/kJ mol^{-1} $\simeq -253.2x - 360.1$ for which $R^2 = 0.999$, $N = 3$ (item 2).

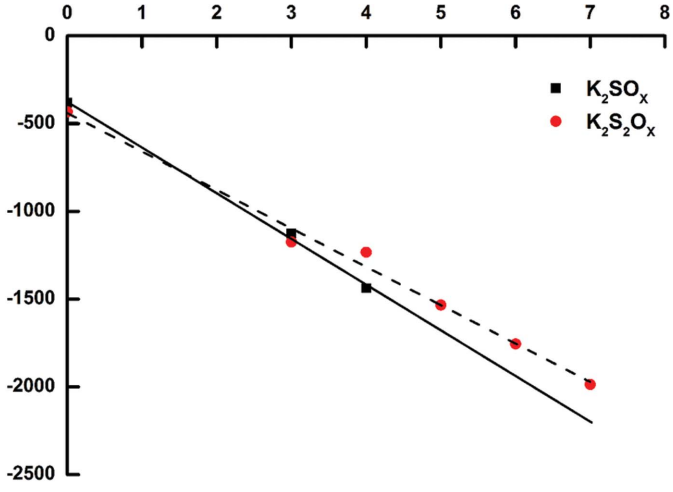

Figure 4
Plots of $\Delta_fH^o(K_2S_2O_x,c)$/kJ mol^{-1} ($x = 0, 3, 4, 5, 6, 7$) as ordinate *versus* x as the abscissa (dotted line), and $\Delta_fH^o(K_2SO_x,c)$/kJ mol^{-1} ($x = 0, 4, 5, 6$) as ordinate *versus* x as the abscissa (solid line). Data from Table 2. Least-squares fitted lines take the forms: $\Delta_fH^o(K_2S_2O_x,c)$/kJ mol^{-1} $\simeq -218.4x - 459.2$ for which $R^2 = 0.997$, $N = 5$ (item 8), $\Delta_fH^o(K_2SO_x,c)$/kJ mol^{-1} $\simeq -260.6x - 373.3$ for which $R^2 = 0.998$, $N = 3$ (item 6).

3. Currently unavailable thermodynamic data for well established compounds estimated by interpolation

3.1. Polysulfide oxyanion salts

3.1.1. Enthalpies of formation. We can use the correlation (item 8) summarized in Table 1 to predict the standard enthalpy of formation of dipotassium dithionite, $K_2S_2O_4$. The result is given in Table 2.

3.1.2. Gibbs energy of formation. We use the correlations (item 5) from Table 1 to predict the standard Gibbs energy of formation of disodium metabisulfite (pyrosulfite), $Na_2S_2O_5$. The result is given (in italics) in Table 2.

4. Currently unavailable thermodynamic data for hypothetical salts estimated by interpolation

4.1. Thioperoxides, M_2SO

4.1.1. Enthalpies of formation. Interpolation of the linear plots of $\Delta_fH^o(M_2SO_x,c)$ *versus* x (items 1, 2, 6, 9 and 10 in Table 1) for $x = 1$ leads to the predicted data for Li_2SO, Na_2SO, K_2SO, Rb_2SO and Cs_2SO given (in italics) in Table 2.

4.1.2. Gibbs energies of formation. The complete absence (see Table 2) of any Δ_fG^o data for Li salts and the existence of only aqueous data (Wagman *et al.*, 1982) for both Rb and Cs salts [with the exception of single values for $\Delta_fG^o(Rb_2SO_4,c)$ and $\Delta_fG^o(Cs_2SO_4,c)$] prevent the construction of $\Delta_fG^o(M_2SO_x,c)$ *versus* x correspondence plots for these alkali metals so no data for Li_2SO, Rb_2SO or Cs_2SO can be predicted. However, in the case of the disodium and dipotassium salts we interpolate (items 3 and 7 in Table 1) the data listed (in italics) in Table 2.

4.2. Sulfoxylates, M_2SO_2 ($x = 2$)

4.2.1. Enthalpies of formation. Interpolation of the linear plots of Δ_fH^o (M_2SO_x,c) *versus* x (items 1, 2, 6, 9 and 10 in Table 1) for $x = 2$ lead to the predicted data for Li_2SO_2, Na_2SO_2, K_2SO_2, Rb_2SO_2 and Cs_2SO_2 (in italics) in Table 2.

4.2.2. Gibbs energies of formation. For the case of the disodium and dipotassium sulfoxylate salts we find (items 3 and 7 in Table 1) the data listed (in italics) in Table 2.

5. Previous thermodynamics

Previously, the only reference in the literature related to the thermodynamic parameters of alkali metal thioperoxides, M_2SO, and sulfoxylates, M_2SO_2, was embodied in two publications (Ponikvar & Liebman, 2004; Toscano *et al.*, 2003) dealing with aqueous species. Jenkins & Tudela (2003) studied the question of the stability of bisulfites. Although the bisulfites, $MHSO_3$ (M = Li, Na, and K), were widely believed to be stable compounds, they have *never been obtained as solids*. It appeared that the cations, M^+ are insufficiently large enough to stabilize the HSO_3^- ion relative to the metabisulfite, $S_2O_5^{2-}$, ion. These compounds ($MHSO_3$) have had a chequered history. Crystalline compounds, originally thought to be $NaHSO_3$ and $KHSO_3$, were identified by Foerster *et al.* (1924) to be *metabisulfites*, $Na_2S_2O_5$ and $K_2S_2O_5$. Simon & Schmidt (1960) reported the synthesis of $MHSO_3$ salts (M = Rb and Cs), but the contention that these salts contained HSO_3^- anions was challenged (Schmidt & Wirwoll, 1960) because they failed to react with disulfur dichloride in anhydrous tetrahydrofuran to form HCl and $M_2S_4O_6$. It was two decades before Meyer *et al.* (1979) provided convincing spectroscopic evidence for the presence of HSO_3^-, so establishing the salts as being $RbHSO_3$ and $CsHSO_3$. The fact that $RbHSO_3$ and $CsHSO_3$ can be isolated, whilst attempts to crystallize $MHSO_3$ (M = Li, Na, K) led to the formation of $M_2S_2O_5$ (Jenkins *et al.*, 1999) [$2MHSO_3$ (s) $\rightarrow$ $M_2S_2O_5$(s) + H_2O(l)] was explained using VBT (Jenkins & Tudela, 2003). Some additional thermodynamic data supplied by one of our reviewers is incorporated into Table 2.

6. Predicted thermodynamic values for Δ_fH^o and Δ_fG^o for thiosulfoxylate, M_2S_2O, and dithiosulfoxylate, $M_2S_2O_2$, salts

Interpolated values of:

Δ_fH^o (items 4 and 8, Table 1, $x = 1$) and Δ_fG^o (item 5, Table 1, $x = 1$) are listed in Table 2 for thiosulfoxylates.

Δ_fH^o (items 4 and 8, Table 1, $x = 2$) and Δ_fG^o (item 5, Table 1, $x = 2$) are listed (in italics) in Table 2 for dithiosulfoxylates.

7. Estimation of $S^o_{298}(M_2SO,c)$ and $S^o_{298}(M_2SO_2,c)$ for remaining salts using VBT

In Table 2 this work has established data (in italics) for $\Delta_fG^o(M_2SO,c)$, $\Delta_fG^o(M_2SO_2,c)$ (Table 1, items 3 and 7), $\Delta_fH^o(M_2SO,c)$ and $\Delta_fH^o(M_2SO_2,c)$ (Table 1, items 2 and 6) for M = Na and K and for $\Delta_fH^o(M_2SO,c)$ and for

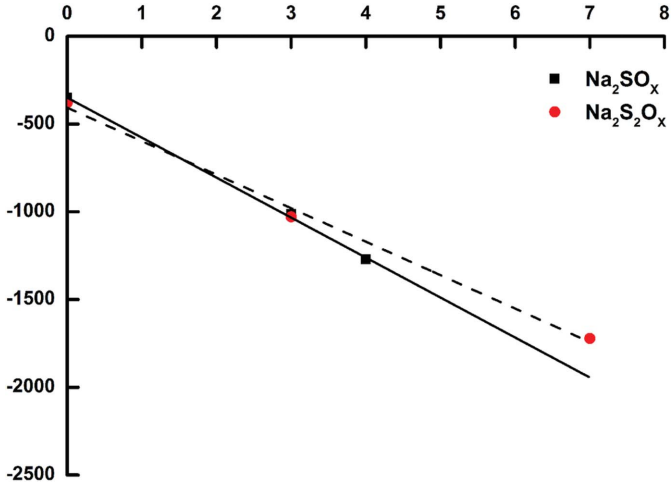

Figure 5
Plots of $\Delta_fG^o(Na_2S_2O_x,c)$/kJ mol^{-1} ($x$ = 0, 3, 7) as ordinate *versus* x as the abscissa (dotted line) and $\Delta_fG^o(Na_2SO_x,c)$/kJ mol^{-1} (x = 0, 3, 4) as ordinate *versus* x as the abscissa (solid line). Data from Table 2. Least-squares fitted lines take the forms: $\Delta_fG^o(Na_2S_2O_x,c)$/kJ mol^{-1} $\simeq -189.6x - 406.9$ for which $R^2 = 0.997$, $N = 4$ (item 5), $\Delta_fG^o(Na_2SO_x,c)$/kJ mol^{-1} $\simeq -228.0x - 345.6$ for which $R^2 = 0.999$, $N = 3$ (item 3).

$\Delta_f H^o(M_2SO_2,c)$ (Table 1, items 1, 9 and 10) for M = Li, Rb and Cs. What is required to do next is to estimate $\Delta_f G^o(M_2SO,c)$ and $\Delta_f G^o(M_2SO_2,c)$ for M = Li, Rb and Cs first by estimating $S^o_{298}(M_2SO,c)$ and $S^o_{298}(M_2SO_2,c)$ and then by estimating $\Delta_f S^o(M_2SO,c)$ and $\Delta_f S^o(M_2SO_2,c)$.

Experimental standard entropy data is only available in Table 2 for the crystalline sulfates of Li, Rb and Cs (*i.e.* only for x = 4) and so no plots similar to those made in Table 1 for other alkali halide salts can be made here.

Table 3
Crystal structure volume data for M_2SO_x and M_2SeO_x salts (x = 0, 3, 4) in nm^3 and estimated volumes for M_2SO_2 and M_2SeO_2 in nm^3 based on the isomegethic rules.

Rules: $V_m(M_2SO_x)$ (nm^3) $\simeq (1 - x/y)V_m(M_2S) + (x/y)V_m(M_2SO_y)$ and $V_m(Na_2SeO_x)$ (nm^3) $\simeq (1 - x/y)V_m(Na_2Se) + (x/y)V_m(Na_2SeO_y)$; y = 1, 2, 3 and 4, but $y \neq x$. Estimated standard absolute entropies, $S^0_{298}(M_2SO_x,c)$ (J K^{-1}mol^{-1}) and $S^0_{298}(Na_2SeO_x,c)$ (J K^{-1} mol^{-1}) for x = 1 and 2, using the Jenkins Glasser equation.

No. of O atoms in anion, x	$V_m(Li_2SO_x,s)$ (nm^3)	$V_m(Na_2SO_x,s)$ (nm^3)	$V_m(K_2SO_x,s)$ (nm^3)	$V_m(Rb_2SO_x,s)$ (nm^3)	$V_m(Cs_2SO_x,s)$ (nm^3)
Sulfoxylates					
0	**Li_2S** *Cubic* *Fm*$\bar{3}$*m*, *Z* = 4 *a* = 0.5708 nm V_m = 0.0464 nm^3 $S^0_{298}(Li_2S,c)$ = 78 ± 15 (J K^{-1}mol^{-1})	**Na_2S** *Cubic* *Fm*$\bar{3}$*m*, *Z* = 4 *a* = 0.6538 nm V_m = 0.0698 nm^3 $S^0_{298}(Na_2S,c)$ = 109 ± 15 (J K^{-1}mol^{-1}) **$Na_2S{\cdot}5H_2O$** *Cmcm*; *Z* = 4 *V* = 0.7052 nm^3 V_m = 0.1763 nm^3 **$Na_2S{\cdot}9H_2O$** $P4_122$; *Z* = 4 *V* = 1.1132 nm^3 V_m = 0.2783 nm^3	**K_2S** *Cubic* *Fm*$\bar{3}$*m*, *Z* = 4 *a* = 0.7405 nm V_m = 0.1010 nm^3 $S^0_{298}(K_2S,c)$ = 152 ± 15 (J K^{-1} mol^{-1})	**Rb_2S** *Cubic* *Fm*$\bar{3}$*m*, *Z* = 4 *a* = 0.765 nm V_m = 0.1119 nm^3 $S^0_{298}(Rb_2S,c)$ = 167 ± 15 (J K^{-1} mol^{-1})	**Cs_2S** Orthorhombic *Pnma*, *Z* = 4 *a* = 0.5383 nm *b* = 0.8571 nm *c* = 1.039 nm V_m = 0.1198 nm^3 $S^0_{298}(Cs_2S,c)$ = 178 ± 15 (J K^{-1} mol^{-1})
1 *Estimated volumes*	**Li_2SO** $\frac{1}{2}V_m(Li_2S) + \frac{1}{2}V_m(Li_2SO_2)$ = 0.0553 nm^3 $\frac{2}{3}V_m(Li_2S) + \frac{1}{3}V_m(Li_2SO_3)$ = 0.0553 nm^3 $\frac{3}{4}V_m(Li_2S) + \frac{1}{4}V_m(Li_2SO_4)$ = 0.0553 nm^3 Average = 0.0553 nm^3 $S^0_{298}(Li_2SO,c)$ = 90.2 ± 15 (J K^{-1} mol^{-1})	**Na_2SO** $\frac{1}{2}V_m(Na_2S) + \frac{1}{2}V_m(Na_2SO_2)$ = 0.0738 nm^3 $\frac{2}{3}V_m(Na_2S) + \frac{1}{3}V_m(Na_2SO_3)$ = 0.0731 nm^3 $\frac{3}{4}V_m(Na_2S) + \frac{1}{4}V_m(Na_2SO_4)$ = 0.0745 nm^3 Average = 0.0738 nm^3 $S^0_{298}(Na_2SO,c)$ = 115.4 ± 15 (J K^{-1}mol^{-1})	**K_2SO** $\frac{1}{2}V_m(K_2S) + \frac{1}{2}V_m(K_2SO_2)$ = 0.1024 nm^3 $\frac{2}{3}V_m(K_2S) + \frac{1}{3}V_m(K_2SO_3)$ = 0.1025 nm^3 $\frac{3}{4}V_m(K_2S) + \frac{1}{4}V_m(Ka_2SO_4)$ = 0.1023 nm^3 Average = 0.1024 nm^3 $S^0_{298}(K_2SO,c)$ = 154.3 ± 15 (J K^{-1} mol^{-1})	**Rb_2SO** $\frac{1}{2}V_m(Rb_2S) + \frac{1}{2}V_m(Rb_2SO_2)$ = 0.1144 nm^3 $\frac{2}{3}V_m(Rb_2S) + \frac{1}{3}V_m(Rb_2SO_3)$ = 0.1147 nm^3 $\frac{3}{4}V_m(Rb_2S) + \frac{1}{4}V_m(Rb_2SO_4)$ = 0.1144 nm^3 Average = 0.1145 nm^3 $S^0_{298}(Rb_2SO,c)$ = 170.7 ± 15 (J K^{-1} mol^{-1})	**Cs_2SO** $\frac{1}{2}V_m(Cs_2S) + \frac{1}{2}V_m(Cs_2SO_2)$ = 0.1253 nm^3 $\frac{2}{3}V_m(Cs_2S) + \frac{1}{3}V_m(Cs_2SO_3)$ = 0.1253 nm^3 $\frac{3}{4}V_m(Cs_2S) + \frac{1}{4}V_m(Cs_2SO_4)$ = 0.1253 nm^3 Average = 0.1253 nm^3 $S^0_{298}(Cs_2SO,c)$ = 185.4 ± 15 (J K^{-1} mol^{-1})
2 *Estimated volumes*	**Li_2SO_2** $\frac{1}{2}V_m(Li_2S) + \frac{1}{2}V_m(Li_2SO_4)$ = 0.0642 nm^3 $\frac{1}{3}V_m(Li_2S) + \frac{2}{3}V_m(Li_2SO_3)$ = 0.0641 nm^3 $2/5V_m(Li_2S) + 2/5V_m(Li_2SO_3) + 1/5V_m(Li_2SO_4)$ = 0.0641 nm^3 Average = 0.0641 nm^3 $S^0_{298}(Li_2SO_2,c)$ = 102.2 ± 15 (J K^{-1} mol^{-1})	**Na_2SO_2** $\frac{1}{3}V_m(Na_2S) + \frac{2}{3}V_m(Na_2SO_3)$ = 0 0765 nm^3 $\frac{1}{2}V_m(Na_2S) + \frac{1}{2}V_m(Na_2SO_4)$ = 0.0792 nm^3 $2/5V_m(Na_2S) + 2/5V_m(Na\ _2SO_3) + 1/5V_m(Na_2SO_4)$ = 0.0776 nm^3 Average = 0.0778 nm^3 $S^0_{298}(Na_2SO_2,c)$ = 120.8 ± 15 (J K^{-1} mol^{-1})	**K_2SO_2** $\frac{1}{3}V_m(K_2S) + \frac{2}{3}V_m(K_2SO_3)$ = 0.1040 nm^3 $\frac{1}{2}V_m(K_2S) + \frac{1}{2}V_m(K_2SO_4)$ = 0.1036 nm^3 $2/5V_m(K_2S) + 2/5V_m(K_2SO_3) + 1/5V_m(K_2SO_4)$ = 0.1038 nm^3 Average = 0.1038 nm^3 $S^0_{298}(K_2SO_2,c)$ = 156.2 ± 15 (J K^{-1} mol^{-1})	**Rb_2SO_2** $\frac{1}{3}V_m(Rb_2S) + \frac{1}{2}V_m(Rb_2SO_4)$ = 0.1168 nm^3 $S^0_{298}(Rb_2SO_2,c)$ = 173.8 ± 15[a] (J K^{-1} mol^{-1})	**Cs_2SO_2** $\frac{1}{2}V_m(Cs_2S) + \frac{1}{2}V_m(Cs_2SO_4)$ = 0.1308 nm^3 $S^0_{298}(Cs_2SO_2,c)$ = 192.9 ± 15[a] (J K^{-1} mol^{-1})
3	**Li_2SO_3** $\frac{1}{2}V_m(Li_2SO_2) + \frac{1}{2}V_m(Li_2SO_4)$ = 0.0731 nm^3 $\frac{1}{4}V_m(Li_2S) + \frac{3}{4}V_m(Li_2SO_4)$ = 0.0730 nm^3 $3/2V_m(Li_2SO_2) - \frac{1}{2}V_m(Li_2S)$ = 0.0731 nm^3 $3V_m(Li_2SO) - 2V_m(Li_2S)$ = 0.0728 nm^3 Average = 0.0730 nm^3 Crystal structure not reported $S^0_{298}(Li_2SO_3,c)$ = 114 ± 15 (J K^{-1} mol^{-1})	**Na_2SO_3** Trigonal *P*$\bar{3}$, *Z* = 2 *a* = 0.5459 nm *c* = 0.6179 nm V_m = 0.0798 nm^3 $S^0_{298}(Na_2SO_3,c)$ = 123.5 ± 15 (J K^{-1} mol^{-1})	**K_2SO_3** Trigonal *P*$\bar{3}$*m*1, *Z* = 2 *a* = 0.5915 nm *c* = 0.6968 Å V_m = 0.1055 nm^3 $S^0_{298}(K_2SO_3,c)$ = 158.5 ± 15 (J K^{-1} mol^{-1})	**Rb_2SO_3** $\frac{1}{2}V_m(Rb_2SO_2) + \frac{1}{2}V_m(Rb_2SO_4)$ = 0.1192 nm^3 $\frac{1}{4}V_m(Rb_2S) + \frac{3}{4}V_m(Rb_2SO_4)$ = 0.1192 nm^3 $3/2V_m(Rb_2SO_2) - \frac{1}{2}V_m(Rb_2S)$ = 0.1193 nm^3 $3V_m(Rb_2SO) - 2V_m(Rb_2S)$ = 0.1194 nm^3 Average = 0.1193 nm^3 Crystal structure not reported $S^0_{298}(Rb_2SO_3,c)$ = 177 ± 15 (J K^{-1} mol^{-1})	**Cs_2SO_3** $\frac{1}{2}V_m(Cs_2SO_2) + \frac{1}{2}V_m(Cs_2SO_4)$ = 0.1363 nm^3 $\frac{1}{4}V_m(Cs_2S) + \frac{3}{4}V_m(Cs_2SO_4)$ = 0.1363 nm^3 $3/2V_m(Cs_2SO_2) - \frac{1}{2}V_m(Cs_2S)$ = 0.1363 nm^3 $3V_m(Cs_2SO) - 2V_m(Cs_2S)$ = 0.1363 nm^3 Average = 0.1363 nm^3 Crystal structure not reported $S^0_{298}(Cs_2SO_3,c)$ = 200 ± 15 (J K^{-1} mol^{-1})

Table 3 (continued)

No. of O atoms in anion, x	$V_m(Li_2SO_x,s)$ (nm^3)	$V_m(Na_2SO_x,s)$ (nm^3)	$V_m(K_2SO_x,s)$ (nm^3)	$V_m(Rb_2SO_x,s)$ (nm^3)	$V_m(Cs_2SO_x,s)$ (nm^3)
4	**Li_2SO_4** Monoclinic $P2_1/c$, $Z = 4$ $a = 0.845$ nm $b = 0.495$ nm $c = 0.821$ nm $V_m = 0.0819$ nm^3 $S^0_{298}(Li_2SO_4,c) = 126.4 \pm 15$ (J K^{-1} mol^{-1}) **$Li_2SO_4{\cdot}H_2O$** $P2_1$; $Z = 2$ $V = 0.2073$ $V_m = 0.1037$ nm^3 Pyroelectric	**Na_2SO_4** Orthorhombic $Fddd$, $Z = 8$ $a = 0.9821$ nm $b = 1.2307$ nm $c = 0.5862$ nm $V_m = 0.0886$ nm^3 $S^0_{298}(Na_2SO_4,c) = 135.5 \pm 15$ (J K^{-1} mol^{-1}) **$Na_2SO_4{\cdot}10H_2O$** $P12_1/c1$, $Z = 4$ $V = 1.460$ nm^3 $V_m = 0.3650$ nm^3	**K_2SO_4** Orthorhombic $Pnma$, $Z = 4$ $a = 0.5723$ nm $b = 0.9998$ nm $c = 0.7421$ nm $V_m = 0.1062$ nm^3 $S^0_{298}(K_2SO_4,c) = 159.4 \pm 15$ (J K^{-1} mol^{-1})	**Rb_2SO_4** Orthorhombic $Pnma$, $Z = 4$ $a = 0.780$ nm $b = 1.040$ nm $c = 0.600$ nm $V_m = 0.1217$ nm^3 $S^0_{298}(Rb_2SO_4,c) = 180.5 \pm 15$ (J K^{-1} mol^{-1})	**Cs_2SO_4** Orthorhombic $Pnma$, $Z = 4$ $a = 0.625$ nm $b = 1.096$ nm $c = 0.828$ nm $V_m = 0.1418$ nm^3 $S^0_{298}(Cs_2SO_4,c) = 207.8 \pm 15$ (J K^{-1} mol^{-1})

Sodium selenoxylates					
$NaSeO_x$	**Na_2Se** Antifluorite; $Z = 4$ $V = 0.3179$ nm^3 $V_m = 0.0795$ nm^3 $S^0_{298}(Na_2Se,c) = 123 \pm 15$ (J K^{-1} mol^{-1})	**Na_2SeO_2** $\frac{1}{2}V_m(Na_2Se) + \frac{1}{2}V_m(Na_2SeO_4, RT) = 0.0886$ nm^3 $\frac{1}{3}V_m(Na_2Se) + \frac{2}{3}V_m(Na_2SeO_3) = 0.0826$ nm^3 $2/5V_m(Na_2Se) + 2/5V_m(Na_2SeO_3) + 1/5V_m(Na_2SeO_4) = 0.0850$ nm^3 Average $= 0.0854$ nm^3 $S^0_{298}(Na_2SeO_2,c) = 131 \pm 15$ (J K^{-1}mol^{-1})	**Na_2SeO_3** $P2_1/c$; $Z = 4$ $V = 0.3366$ nm^3 $V_m = 0.0842$ nm^3 $S^0_{298}(Na_2SeO_3,c) = 129 \pm 15$ (J K^{-1} mol^{-1})	**Na_2SeO_4 HT**; $Pnma$; $Z = 4$ $V = 0.3766$ nm^3 $V_m = 0.0942$ nm^3 $S^0_{298}(Na_2SeO_4,c) = 143 \pm 15$ (J K^{-1} mol^{-1}) **Na_2SeO_4 RT** $Fddd$; Z= 8 $V = 0.7804$ nm^3 $V_m = 0.0976$ nm^3 $S^0_{298}(Na_2SeO_4,c) = 148 \pm 15$ (J K^{-1} mol^{-1})

We now employ VBT (Jenkins *et al.*, 1999; Jenkins, 2008, 2009; Glasser & Jenkins, 2011*b*) in order to obtain an estimate of standard entropies for the salts in question.

Table 3 assembles crystal structure data for volumes of M_2SO_x salts ($x = 0, 3, 4$) from which, using three forms of the isomegethic rule (Jenkins *et al.*, 2004), we have, in general

$$V_m(M_2SO_x) \simeq (1 - x/y) \cdot V_m(M_2S) + x/y \cdot V_m(M_2SO_y) \quad (1)$$

for $y = 1, 2, 3, 4$, but with the restriction that $y \neq x$. Specifically this means that

$$V_m(M_2SO) \simeq \frac{1}{2}V_m(M_2S) + \frac{1}{2}V_m(M_2SO_2) \quad (2)$$

$$V_m(M_2SO) \simeq \frac{2}{3}V_m(M_2S) + \frac{1}{3}V_m(M_2SO_3) \quad (3)$$

$$V_m(M_2SO) \simeq \frac{3}{4}V_m(M_2S) + \frac{1}{4}V_m(M_2SO_4) \quad (4)$$

$$V_m(M_2SO_2) \simeq 2/5V_m(M_2S) + 2/5V_m(M_2SO_3) + 1/5V_m(M_2SO_4) \quad (5)$$

$$V_m(M_2SO_2) \simeq \frac{1}{3}V_m(M_2S) + \frac{2}{3}V_m(M_2SO_3) \quad (6)$$

$$V_m(M_2SO_2) \simeq \frac{1}{2}V_m(M_2S) + \frac{1}{2}V_m(M_2SO_4) \quad (7)$$

leading *via* the Jenkins Glasser Entropy equation (Jenkins & Glasser, 2003)

$$S^o_{298}(M_2SO_x, c) \simeq kV_m(M_2SO_x, c) + c \ (x = 1, 2), \quad (8)$$

where k (J K^{-1} mol^{-1} nm^{-3}) = 1360 and c (J K^{-1} mol^{-1}) = 15 leading to the values listed in Table 3.

The results for $S^o_{298}(Li_2SO,c)$, $S^o_{298}(Rb_2SO,c)$, $S^o_{298}(Cs_2SO,c)$, $S^o_{298}(Li_2SO_2,c)$, $S^o_{298}(Rb_2SO_2,c)$, $S^o_{298}(Cs_2SO_2,c)$, $S^o_{298}(Li_2SO_3,c)$, $S^o_{298}(Rb_2SO_3,c)$ and $S^o_{298}(Cs_2SO_3,c)$ are given (in italics) in Table 2, which, in turn, when substituted into the equations

$$\Delta_f S^o_{298}(M_2SO, c) \simeq S^o_{298}(M_2SO, c) - 2S^o_{298}(M, c) - S^o_{298}(S, \text{rhombic}, c) - \frac{1}{2}S^o_{298}(O_2, g) \quad (9)$$

$$\Delta_f S^o_{298}(M_2SO_2, c) \simeq S^o_{298}(M_2SO_2, c) - 2S^o_{298}(M, c) - S^o_{298}(S, \text{rhombic}, c) - S^o_{298}(O_2, g) \quad (10)$$

$$\Delta_f S^o_{298}(M_2SO_3, c) \simeq S^o_{298}(M_2SO_3, c) - 2S^o_{298}(M, c) - S^o_{298}(S, \text{rhombic}, c) - 3/2S^o_{298}(O_2, g) \quad (11)$$

leads us to the estimates (in units of J K^{-1} mol^{-1} and with errors of $\pm$ 15 J K^{-1} mol^{-1}): $\Delta_f S^o(Li_2SO,c) \simeq -102$, $\Delta_f S^o(Rb_2SO,c) \simeq -116$, $\Delta_f S^o(Cs_2SO,c) \simeq -119$, $\Delta_f S^o(Li_2SO_2,c) \simeq -193$, $\Delta_f S^o(Rb_2SO_2,c) \simeq -216$, $\Delta_f S^o(Cs_2SO_2,c) \simeq -214$, $\Delta_f S^o(Li_2SO_3,c) \simeq -284$, $\Delta_f S^o(Rb_2SO_3,c) \simeq -377$ and $\Delta_f S^o(Cs_2SO_3,c) \simeq -310$.

By means of a simple calculation in the supplementary material[1] (§S.1) of this paper, we show that if there is an uncertainty in the calculated value of $S^o_{298}(M_2SO_x,c)$ by say, z% (possibly due to the use of our approximate equation to estimate S^o_{298}), then the propagated uncertainty in the value of $\Delta_f S^o(M_2SO_x,c)$, say y%, is smaller, such that $y << z$.

Continuing our calculation

$$\Delta_f G^o = \Delta_f H^o - T\Delta_f S^o \quad (12)$$

so that we estimate the $\Delta_f G^o$ values for the salts listed, as given in Table 2.

No experimental values are listed in Table 1 for $\Delta_f G^o(Rb_2S,c)$ or $\Delta_f G^o(Cs_2S,c)$. To complete the data set we estimate these here. Since (Jenkins *et al.*, 1999) $V(Rb^+)/nm^3 = 0.01386$, $V(Cs^+)/nm^3 = 0.01882$ and $V(S^{2-})/nm^3 = 0.067 \pm 0.019$, then $S^o_{298}(M_2S)$/J K^{-1} mol^{-1} can be estimated from the sulfide equivalent of equation (8) and is given in Table 2. Alternatively, we can use Latimer's approach (Latimer, 1961), using his Tables 87 and 90, which leads to values of $S^o_{298}(M_2S)$/J K^{-1} mol^{-1}, as listed in Table 2. The average of the latter two values is also listed in Table 2. Since

$$\Delta_f S^o_{298}(M_2S, c) \simeq S^o_{298}(M_2S, c) - 2S^o_{298}(M, c) - S^o_{298}(S, \text{rhombic}, c) \simeq S^o_{298}(M_2S, c) - 2S^o_{298}(M, c) - 32.1, \quad (13)$$

then for M = Rb, $\Delta_f S^o_{298}(Rb_2S,c) \simeq -47 \pm 15$ J K^{-1} mol^{-1} and for M = Cs, $\Delta_f S^o_{298}(Cs_2S,c) \simeq -50 \pm 15$ J K^{-1} mol^{-1} which lead to the values for $\Delta_f G^o(Rb_2S,c)$ and $\Delta_f G^o(Cs_2S,c)$ listed in Table 2 *via* equation (12).

8. General remarks concerning prediction of synthesis using thermodynamic considerations

Successful prediction, ahead of synthesis, of inorganic compounds using thermodynamics is not too common an occurrence in chemistry and may be regarded by some as highly speculative and not, therefore, rightfully the subject of a modern crystal chemistry journal. In defence of our decision to explore this area (mainly in the supplementary material) firstly we would argue that it does happen occasionally. Indeed it was the topic of Bill Dasent's excellent book (Dasent, 1965) '*Non–Existent Compounds*' which sparked much exploratory work. Secondly we would point to a study made by Finch, Gates and Jenkins in a series of papers (Finch *et al.*, 1980; Jenkins *et al.*, 1982, 1994; Finch *et al.*, 1993; Jenkins *et al.*, 1996) of the thermodynamics of the PCl_4^+ and PCl_6^- gaseous ions. Their investigation of the likely stability of $MPCl_6$ compounds (M = alkali metal) and their prediction (ahead of synthesis) that $CsPCl_6$ would be the *only* stable alkali metal salt was proven following the synthesis of this salt by Muir (1993), after several abortive attempts at doing so. Recently Hao *et al.* (2007), using energy-resolved, collision-induced, ion-beam mass spectrometry, have determined experimentally $\Delta_f H^o(PCl_4^+, g)$ and the result agrees well with the theoretical predictions made earlier (Jenkins *et al.*, 1994, 1996). A similar result for $\Delta_f H^o(PCl_4^+, g)$ – again in agreement with the experimentally determined value (Hao *et al.*, 2007) – can be generated very simply using VBT (Jenkins *et al.*, 1999; Jenkins, 2008, 2009; Glasser & Jenkins, 2011*b*). This result goes a long way to establishing credibility to this new genre of thermodynamics which is employed in this paper.

Notable too was the success of VBT (Jenkins, 2009) and more extended methods (Dixon *et al.*, 2004) of predicting that the highly publicized (Der Spiegel, Scientific American, *etc*.) and potentially environmentally friendly rocket propellant, N_5N_3 azide, was actually unpreparable.

Thirdly, we would point out that one of the more recent advances that has made the examination of the thermodynamics involved with new potential inorganic syntheses easier, has been the development of the isomegethic principle (Jenkins *et al.*, 2004). This rule enables the estimation of volumes for materials for which no crystal structure data or density data has yet been reported and, used in conjunction with VBT (Jenkins *et al.*, 1999; Jenkins, 2008, 2009; Glasser & Jenkins, 2011*b*), leads to the possibility of estimating otherwise elusive thermodynamics. Indeed, this is a key principle, used in the present paper, which permits us to explore the thermodynamics of the thioperoxides and sulfoxylates. In view of these earlier successes, we feel reasonably confident that attempts to prepare disodium selenoxylate, Na_2SeO_2, the compound on which attention is focused within this main paper, will eventually prove successful. In discussing the stability of inorganic materials, however, we have to add a caveat, urge some caution, and recognize that a system can be apparently stable *thermodynamically* and yet *kinetic* changes may still be taking place, albeit slowly, in some cases, which can prevent the formation of the target material.

9. Investigation of thermodynamic feasibility of selected synthetic routes to obtain sulfoxylates, M_2SO_2

As mentioned above, Vegas (2000, 2011) and Vegas & García-Baonza (2007) have suggested a possible anti-fluorite structure for Na_2SO_2 in which the S atoms would form the f.c.c. array with the alkali metal atoms at the tetrahedral positions,

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: EB5016). Services for accessing these data are described at the back of the journal.

just as found in Na_2S itself. The problem arises that the positions of the O atoms cannot be predicted so until a suitable synthesis is achieved for this salt (or a suitable analogue) and a crystal structure determination be performed, his prediction cannot be tested. The reason being that the SO_2 groups cannot be accommodated at the cell origin, as in the fluorite-type Na_2S, because that Wyckoff site lies on a three-fold axis, a site symmetry that cannot be satisfied by a SO_2 group unless the O atoms were located in a higher occupancy site with a fractional occupancy factor (*s.o.f.* less than 1). Another possibility is to lower the symmetry of the Na_2SO_2 structure until the SO_2 groups can be located either at binary axes or at mirror planes.

This does not prevent us estimating the thermodynamics since the problem of having insufficiently detailed structural information is circumvented by the use of VBT (Jenkins *et al.*, 1999; Jenkins, 2008, 2009; Glasser & Jenkins, 2011*b*), since structural features are not required in this approach. However, the motivation to study the compound remains.

We consider briefly here the possible synthesis of alkali metal sulfoxylates, particularly of the disodium salt. Having secured (see Table 2) estimates of $\Delta_f G^o(M_2SO_2,c)$ for M = alkali metal we can now investigate the thermodynamics of their reactions and comment on the likely feasibility of their syntheses.

9.1. Synthesis of Na_2SO_2 from Na_2O_2 and rhombic sulfur

As has been mentioned above, the synthesis of Na_2SO_2 was attempted by Jansen & Wiench – as reported by Wiench (1975) – who tried to obtain the compound by *heating* disodium peroxide with sulfur, in a sealed ampoule under vacuum.

$$Na_2O_2(c) + S(\text{rhombic}, c) \rightarrow Na_2SO_2(c) \qquad (14)$$

At ambient temperatures we might predict thermodynamically that this reaction (14) is favoured, since

$$\begin{aligned}\Delta G^o(14) &= \Delta_f G^o(Na_2SO_2, c) \\ &\quad - \Delta_f G^o(Na_2O_2, c) \\ &\quad - \Delta_f G^o(S, \text{rhombic}, c) \\ &= (-802 \pm 22) - (-447.7) - (0)\ \text{kJ mol}^{-1} \\ &= -354 \pm 22\ \text{kJ mol}^{-1}. \end{aligned} \qquad (15)$$

Data are taken from Wagman *et al.* (1982) and from Karapet'yants & Karapet'yants (1970). This synthesis was, however, *not* successful.

Preparation of the corresponding dipotassium-based sulfoxylate by a similar route involves dipotassium peroxide, K_2O_2, for which $\Delta_f G^o(K_2O_2,c)/\text{kJ mol}^{-1} = -428.5$ (Barin, 1993) and forming K_2SO_2 as the target salt, the corresponding reaction has $\Delta G^o/\text{kJ mol}^{-1} = -406$, and appears to be slightly (*ca* 50 kJ mol^{-1}) more thermodynamically favoured than Na_2SO_2 formation.

9.2. Temperature dependence of the thermodynamics of synthesis of Na_2SO_2 from Na_2O_2 and S

In order to investigate behaviour at temperatures other than 298 K of any of our proposed synthetic reactions we need to know how $\Delta_f G^o(M_2SO_2,c)$ varies with temperature, T. Essentially this means repeating the interpolation procedure described earlier at other temperatures. Provided linear plots are obtained at these other temperatures we can proceed as before. Using available data (Barin, 1993) for $\Delta_f G^o(Na_2S,c)$, $\Delta_f G^o(Na_2SO_3,c)$ and $\Delta_f G^o(Na_2SO_4,c)$ at temperatures between 300 and 700 K, and plotting this against x, we do indeed find linear behaviour with R^2 consistently 0.998 or 0.999. Generalizing, the empirical results give

$$\begin{aligned}\Delta_f G^o_T(Na_2SO_x, c)/\text{kJ mol}^{-1} &\simeq [0.064(T/\text{K}) - 239.0]x \\ &\quad + [0.1392(T/\text{K}) - 415.7]\end{aligned} \qquad (16)$$

for $300 < T/\text{K} < 700$ and specifically for disodium sulfoxylate, Na_2SO_2, when $x = 2$ this gives

$$\Delta_f G^o_T(Na_2SO_2, c)/\text{kJ mol}^{-1} \simeq [0.2672(T/\text{K}) - 893.6], \qquad (17)$$

which expresses the Gibbs energy of formation of the hypothetical salt as a function of temperature, T (K).

Using equation (17) we can now write a temperature-dependent equation for ΔG^o for reaction (14) at any temperature, provided we have the associated data for $\Delta_f G^o_T(Na_2O_2,c)/\text{kJ mol}^{-1}$ for the same temperature range. The latter data when plotted against temperature, taking values at 300, 400, 500, 600 and 700 K (Barin, 1993) conforms to a linear plot ($R^2 = 1$, $N = 5$) and leads to

$$\Delta_f G^o_T(Na_2O_2, c)/\text{kJ mol}^{-1} \simeq [0.2227(T/\text{K}) - 516.5], \qquad (18)$$

whereupon for reaction (14)

$$\begin{aligned}\Delta G^o_T(14)/\text{kJ mol}^{-1} &\simeq [0.2672(T/\text{K}) \\ &\quad - 893.6] - [0.2227(T/\text{K}) - 516.5] \\ &\simeq [0.0445(T/\text{K}) - 377.3].\end{aligned} \qquad (19)$$

The rather low magnitude of the coefficient of the temperature-dependent term in equation (19) suggests a weak temperature dependence of $\Delta G^o_T(14)$, in that between 300 and 700 K we witness only a 9 kJ mol^{-1} change (from -354 kJ mol^{-1} at 298 K to -345 kJ mol^{-1} at 700 K).

We have to conclude that other factors (see below) must have prevented Jansen's synthesis of Na_2SO_2 from disodium peroxide and sulfur by route (14).

9.3. Alternative synthesis of Na_2SO_2 from Na metal and sulfur dioxide gas

We propose here that a preferable route to successful synthesis might be by means of a low-temperature route. Clearly we need a medium for the sodium, since interacting gas directly with solid (however reactive) would create a surface reaction. However dissolving sodium in liquid ammonia would mean we could bubble SO_2 gas through it and

Table 4
Likely thermodynamic stability of M_2SO_2 salts.

M	$\Delta_fG^o(M_2SO_4,c)$ (kJ mol^{-1})	$\Delta_fG^o(M_2S,c)$ (kJ mol^{-1})	$\Delta_fG^o(M_2SO_2,c)$ (kJ mol^{-1})	$\Delta_fG^o(24)$ (kJ mol^{-1})	Conclusion about stability Likely error in $\Delta G^o(24)$(kJ mol^{-1})
Li	−1321.8	−436.1	−878 ± 9	+1.7	Li_2SO_2 exhibits borderline stability ± 11
Na	−1270.2	−349.8	−802 ± 9	−16.0	Na_2SO_2 appears to be unstable ± 13
K	−1321.4	−364.0	−853 ± 18	+20.6	Along with Cs_2SO_2, K_2SO_2 emerges as a stable salt ± 25
Rb	−1317.0	−350 ± 8	−833 ± ?	+0.9	Rb_2SO_2 exhibits borderline (knife- edge) stability > 8
Cs	−1323.7	−348 ± 8	−826 ± 11	+19.7	Along with K_2SO_2, Cs_2SO_2 emerges as a stable salt ± 17

thermodynamics says this is a favourable reaction using the analysis below. The reaction is

$$2\text{Na(liquid ammonia)} + SO_2(g) \rightarrow Na_2SO_2(c), \qquad (20)$$

for which

$$\begin{aligned}\Delta G^o(20) &= \Delta_fG^o(Na_2SO_2, c)\\ &\quad - 2\Delta_fG^o(\text{Na, liquid ammonia})\\ &\quad - \Delta_fG^o(SO_2, g)\\ &= (-802 \pm 9)\\ &\quad - 2\Delta_fG^o(\text{Na, liquid ammonia})\\ &\quad - (-300.1)\\ &= [-502 - 2\Delta_fG^o(\text{Na, liquid ammonia})]\\ &\quad \pm 9\,\text{kJ mol}^{-1}. \qquad (21)\end{aligned}$$

The value of Δ_fG^o(Na, liquid ammonia) is not immediately available. However, we can estimate Δ_fH^o(Na, liquid ammonia) by extrapolating data for Δ_fH^o of Na in liquid NH_3 at a variety of concentrations (see Fig. 6) to an infinite ammonia concentration. This will then approximate closely to Δ_fH^o(Na, liquid ammonia). We find

$$\Delta_fH^o(\text{Na, liquid ammonia})/\text{kJ mol}^{-1} \rightarrow -2.0. \qquad (22)$$

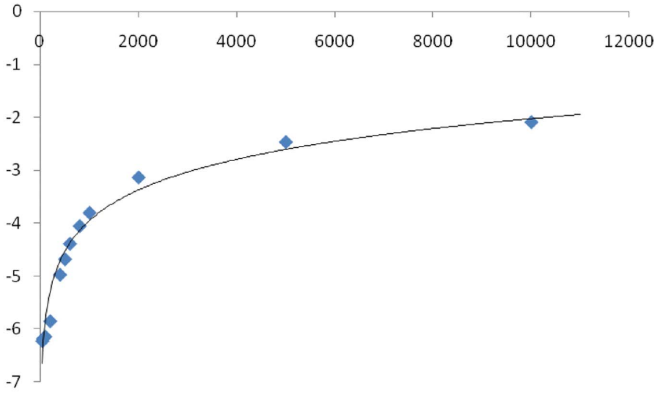

Figure 6
Plots of Δ_fH^o(Na in n NH_3)/kJ mol^{-1} *versus* n showing that extrapolation to infinite n (corresponding to pure liquid ammonia) gives a value for Δ_fH^o(Na, liquid ammonia)/kJ mol^{-1} approximating to −2.00. Data from NBS tables (Wagman *et al.*, 1982).

This in turn means that Δ_fG^o(Na, liquid ammonia) is also likely to be very small in magnitude and thus when inserted into equation (21) will lead to

$$\Delta G^o(22)/\text{kJ mol}^{-1} \simeq -502 \pm 9, \qquad (23)$$

and so we conclude that this present route is more thermodynamically favoured than the previous route, in addition to the fact that this synthetic route provides a suitable solvent medium in which to carry out the synthesis.

10. Thermodynamic stability of disodium sulfoxylate, Na_2SO_2, and other sulfoxylates

10.1. Possible decomposition of sulfoxylates

Were a sulfoxylate, M_2SO_2, to be thermodynamically *unstable* once synthesized, then the decomposition mode in equation (24) represents what is probably the most likely route for such instability. Such a route arises because the corresponding alkali metal sulfide and sulfate salts are highly stable materials. Thus, the reaction

$$2M_2SO_2(c) \rightarrow M_2S(c) + M_2SO_4(c) \qquad (24)$$

must be examined, for which $\Delta G^o(24)$ is given by

$$\begin{aligned}\Delta G^o(24) &= \Delta_fG^o(M_2SO_4, c)\\ &\quad + \Delta_fG^o(M_2S, c) - 2\Delta_fG^o(M_2SO_2, c). \qquad (25)\end{aligned}$$

Table 4 uses the estimated and experimental data from Table 2 to probe the stability of the alkali metal sulfoxylates. If $\Delta G^o(24) > 0$ the decomposition reaction for M_2SO_2 will *not* proceed and the sulfoxylate will be thermodynamically stable; if, however $\Delta G^o(24) < 0$ the decomposition reaction for M_2SO_2 is likely and the sulfoxylate will then be thermodynamically unstable and would disproportionate on synthesis; in the case where $\Delta G^o(24) \simeq 0$ the sulfoxylate will have knife-edge stability. As a further consideration we must also bear in mind the uncertainties associated with the magnitude of $\Delta G^o(24)$ in each case. $\Delta G^o(24)$ is given in column 5 of Table 4.

10.2. Conclusions concerning sulfoxylate stabilities

The data in columns 2, 3, 4 and 5 of Table 4 do not follow smooth variation as we progress down the series from Li to Cs.

Table 5
Variation of free energy data down an alkali metal series for selected salts (Wagman *et al.*, 1982).

M	$\Delta_fG^o(M_2CO_3,c)$ (kJ mol^{-1})	$\Delta_fG^o(M_2O_2,c)$ (kJ mol^{-1})	$\Delta_fG^o(M\mathrm{H},c)$ (kJ mol^{-1})	$\Delta_fG^o(M\mathrm{NO_3},c)$ (kJ mol^{-1})	$\Delta_fG^o(M\mathrm{NO_2},c)$ (kJ mol^{-1})
Li	−1132.1	−571.0[a]	−68.3	−381.1	−302.0
Na	−1044.4	−447.7	−33.5	−367.0	−284.6
K	−1063.5	−425.1 −428.5[a]	−34.0[a]	−394.9	−306.6
Rb	−1051.0	–	–	−395.8	−306.2
Cs	–	–	–	–	–

References: (*a*) Barin (1993).

It is largely for this reason that the resultant values for $\Delta G^o(24)$ are somewhat erratic. The value of $\Delta G^o(24)$ for Na_2SO_2, for example, seems oddly positive when all the other alkali metal results are negative; the trends do not seem quite as might be expected. However, a smooth variation for sodium Δ_fG^o data within an alkali metal series is not, in fact, expected as the collected data for various alkali metal salts in Table 5 illustrates. Given then that our data seems to conform to other exhibited trends, we conclude:

(i) that Na_2SO_2 emerges as likely to be **unstable** towards disproportionation to the sulfide and sulfate;

(ii) that whilst Li_2SO_2 and Rb_2SO_2 have precarious borderline stabilities, potassium and dicesium sulfoxylates appear to be the two salts most likely to be preparable and stable;

(iii) that K_2SO_2 and Cs_2SO_2 emerge as the two salts most likely to be preparable and **stable**;

(iv) that uncertainties found for $\Delta G^o(24)$ (which are particularly large for K_2SO_2 and for Cs_2SO_2) make these assignments of stability tentative.

11. Disodium selenoxylate

11.1. Synthesis of Na_2SeO_2 from Na metal (in liquid ammonia) and solid selenium dioxide

In view of the uncertainty concerning the instability of disodium sulfoxylate, we need to consider the stability and preparation of a suitable crystallographic alternative compound in order to test our structural prediction. Disodium selenoxylate, Na_2SeO_2, selenium being the Group 16 element below sulfur, is such a suitable compound and it also appears to have a number of thermodynamic/synthetic advantages over Na_2SO_2 for the following reasons. Whereas SO_2 is a gas, SeO_2 is a *solid* material which could be reacted more easily with Na in liquid ammonia. So, practically, this might represent a facile synthesis. $\Delta_fG^o(SeO_2,c)$/kJ mol^{-1} = −171.471 (Table 2) so that the reaction

$$2\mathrm{Na(liquid\,NH_3},\,l) + \mathrm{SeO_2}(c) \rightarrow \mathrm{Na_2SeO_2}(c) \qquad (26)$$

has a large and negative free energy change

$$\begin{aligned}\Delta G^o(26) &= \Delta_fG^o(\mathrm{Na_2SeO_2},\,c) - \Delta_fG^o(\mathrm{SeO_2},\,c) \\ &\quad - 2\Delta_fG^o(\mathrm{Na,\ liquid\ ammonia}) \\ &\simeq (-738 \pm 8) - (-171.471) - (-2)\,\mathrm{kJ\,mol^{-1}} \\ &= -563 \pm 8\,\mathrm{kJ\,mol^{-1}}. \end{aligned} \qquad (27)$$

Since $\Delta G^o(29) < \Delta G^o(22)$ the Na_2SeO_2 preparation is *even more thermodynamically* favoured than the corresponding one for Na_2SO_2.

11.2. Synthesis of Na_2SeO_2 from Na metal and solid selenium dioxide

Direct reaction of powdered SeO_2 with sodium metal can also present a favourable reaction

$$2\mathrm{Na}(c) + \mathrm{SeO_2}(c) \rightarrow \mathrm{Na_2SeO_2}(c) \qquad (28)$$

which has a large and negative free energy change

$$\begin{aligned}\Delta G^o(28) &= \Delta_fG^o(\mathrm{Na_2SeO_2},\,c) - \Delta_fG^o(\mathrm{SeO_2},\,c) \\ &\quad - 2\Delta_fG^o(\mathrm{Na},\,c) \\ &\simeq (-738 \pm 8) \\ &\quad - (-171.471) - (0) \\ &= -566 \pm 8\,\mathrm{kJ\,mol^{-1}}. \end{aligned} \qquad (29)$$

11.3. Synthesis of Na_2SeO_2 from sodium peroxide, Na_2O_2 and selenium

Although less practically useful as a preparative route (by virtue of a surface reaction possibly slowing the kinetics) the reaction of powdered selenium metal with sodium peroxide

$$\mathrm{Na_2O_2}(c) + \mathrm{Se}(c) \rightarrow \mathrm{Na_2SeO_2}(c) \qquad (30)$$

also has a large and negative free energy change

$$\begin{aligned}\Delta G^o(30) &= \Delta_fG^o(\mathrm{Na_2SeO_2},\,c) \\ &\quad - \Delta_fG^o(\mathrm{Na_2O_2},\,c) \\ &\quad - \Delta_fG^o(\mathrm{Se},\,c) \\ &\simeq (-738.3 \pm 8) - (-447.7) - (0)\,\mathrm{kJ\,mol^{-1}} \\ &= -303 \pm 8\,\mathrm{kJ\,mol^{-1}}. \end{aligned} \qquad (31)$$

11.4. Thermodynamic stability of Na_2SeO_2

Finally, with regard to the stability of Na_2SeO_2 and its possible disproportionation to selenide and selenate

$$2Na_2SeO_2(c) \rightarrow Na_2Se(c) + Na_2SeO_4(c), \qquad (32)$$

which is seen to be thermodynamically forbidden

$$\begin{aligned}\Delta G^{o}(32) &= \Delta_f G^{o}(Na_2SeO_4, c) \\ &\quad + \Delta_f G^{o}(Na_2Se, c) \\ &\quad - 2\Delta_f G^{o}(Na_2SeO_2, c) \\ &\simeq (-941.7) + (-339.9) - 2(-738 \pm 8)\ \text{kJ mol}^{-1} \\ &= +194 \pm 11\ \text{kJ mol}^{-1}. \qquad (33)\end{aligned}$$

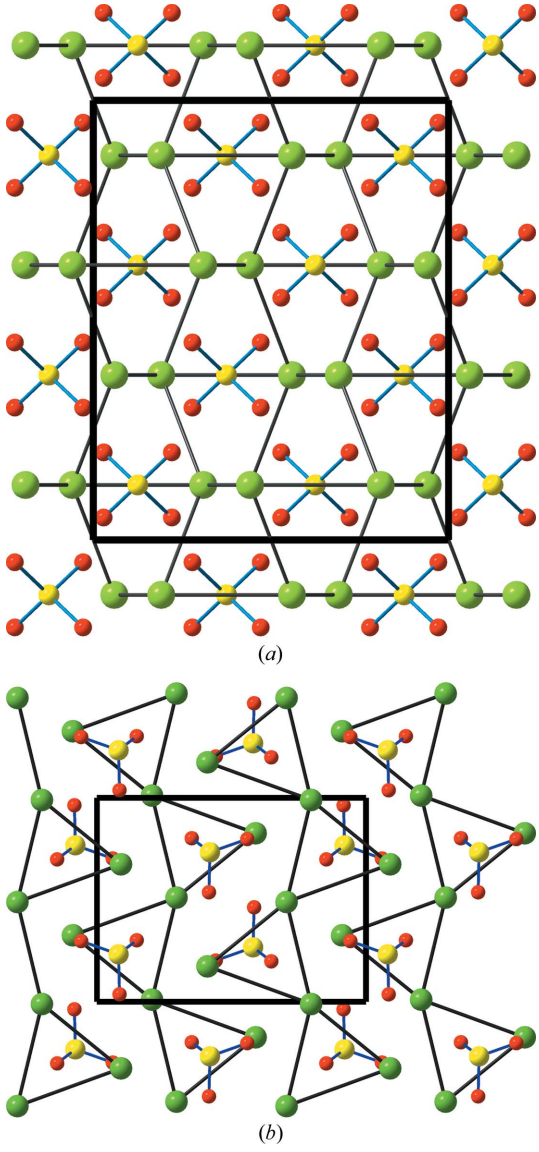

Figure 7
(*a*) The structure of room-temperature Na_2SeO_4 (*Fddd*), which is of the thenardite-type. (*b*) The high-temperature phase of Na_2SeO_4 (*Pnma*). The SeO_4 tetrahedra lie at the centre of the Na_6 trigonal prisms. Na: green; Se: yellow; O: red.

The high positive value of $\Delta G^{o}(32)$ ensures the complete stability of the target disodium selenoxylate, Na_2SeO_2.

11.5. Na_2SeO_2 from a crystallographic standpoint

The fact that it appears that we are likely to be able to synthesize a stable Na_2SeO_2 prompts us to analyse the detailed structures of other Na_2SeO_x (x = 3 and 4). At ambient conditions Na_2SeO_4 is isostructural with thenardite (V-Na_2SO_4) (*Fddd*) (Kálmán & Cruickshank, 1970), but at high temperature it transforms into the glasserite-type structure of β-K_2SO_4 (*Pnma*) (Mehrotra *et al.*, 1977). This phase transition which occurs in sodium selenate has not been observed in the corresponding sulfate, which transforms directly from thenardite to I-Na_2SO_4 ($P6_3/mmc$). These phase changes are summarized below (in Path 2) and as will be discussed later, the cation subarrays of these structures correspond to $TiSi_2$, $PbCl_2$ and Ni_2In, respectively.

Fddd	→	*Pnma*	→	$P6_3/mmc$
Na_2SO_4				HT- I-Na_2SO_4
		β-K_2SO_4		HT- K_2SO_4
Na_2SeO_4		HT- Na_2SeO_4		

Path 2

The structures of the two Na_2SeO_4 polymorphs are represented in Fig. 7.

The structure of selenite, Na_2SeO_3 ($P2_1/c$) (Wickleder, 2002), presents us with some peculiarities. If one tries to describe it as a set of trigonal prisms like those existing in Na_2SO_3 they are completely distorted and quite far from that of Na_2SO_3 (*cf.* Figs. 8*a* and *d*). However, the structure is better described as a distorted f.c.c. array formed by both Se and Na atoms (see Fig. 8*b*), as shown by the distorted cubes represented in Fig. 8(*c*).

The important point to make is that in Na_2SO_3 the Na_2S moiety is compressed with respect to the CaF_2-type structure (Vegas, 2011). The Na atoms, as in the CaF_2-type structure, form a simple cubic network in which alternative cubes are filled by F(S) atoms. In Na_2SO_3, however, all the cubes are filled indistinctly by Na and SO_3 groups (see Fig. 6*e*). Thus, Na and S atoms altogether form a b.c.c.-type array. An important aspect of this array is that the cubes filled with the SO_3 groups are in fact oxygen-stuffed Na_8S cubes like those existing in the fluorite structure (see Fig. 1*a* and Fig. 9*a*). This indicates that Na_2SO_3 is close to the fluorite structure and that if the O content is lowered, as in Na_2SO_2, the array should be even closer to that of CaF_2, as we have postulated.

In the heavier Na_2SeO_3 the Na and Se atoms together form a f.c.c. structure (see Fig. 9*c*) which should be considered as having a denser packing than is found in the sulfite. In both cases, the result is as expected and yields cation arrays which are closer to the parent CaF_2-type structures of Na_2S and Na_2Se (Vegas, 2011).

12. Concluding remarks

The provision of missing thermodynamic data for well established polysulfur oxysalts has been readily established in this paper relying on experimental data for $M_2S_2O_x$, where x is in the range $0 \leq x \leq 7$. The $\Delta_f H^o$ values established for thioperoxides and sulfoxylates in Table 2 rely on plots made where $0 \leq x \leq 4$ – a smaller compass of values than for the polysulfur oxy salts – but nevertheless the plots are reliably linear. Only $\Delta_f G^o$ values can robustly be established for the disodium and dipotassium thioperoxides and sulfoxylates. The remaining $\Delta_f G^o$ data, predicted for the Li, Rb and Cs salts, are less certain since they rely on VBT approximate methods (Jenkins *et al.*, 1999; Jenkins, 2008, 2009; Glasser & Jenkins, 2011*b*) to secure values.

The importance of the data provided in this paper is threefold:

(i) It is established, in its own right, as an addition to the (existing) thermochemical literature.

(ii) It further permits us to explore, on thermodynamic grounds, the existence of compounds whose synthesis has not yet been achieved and enables comment on their stabilities.

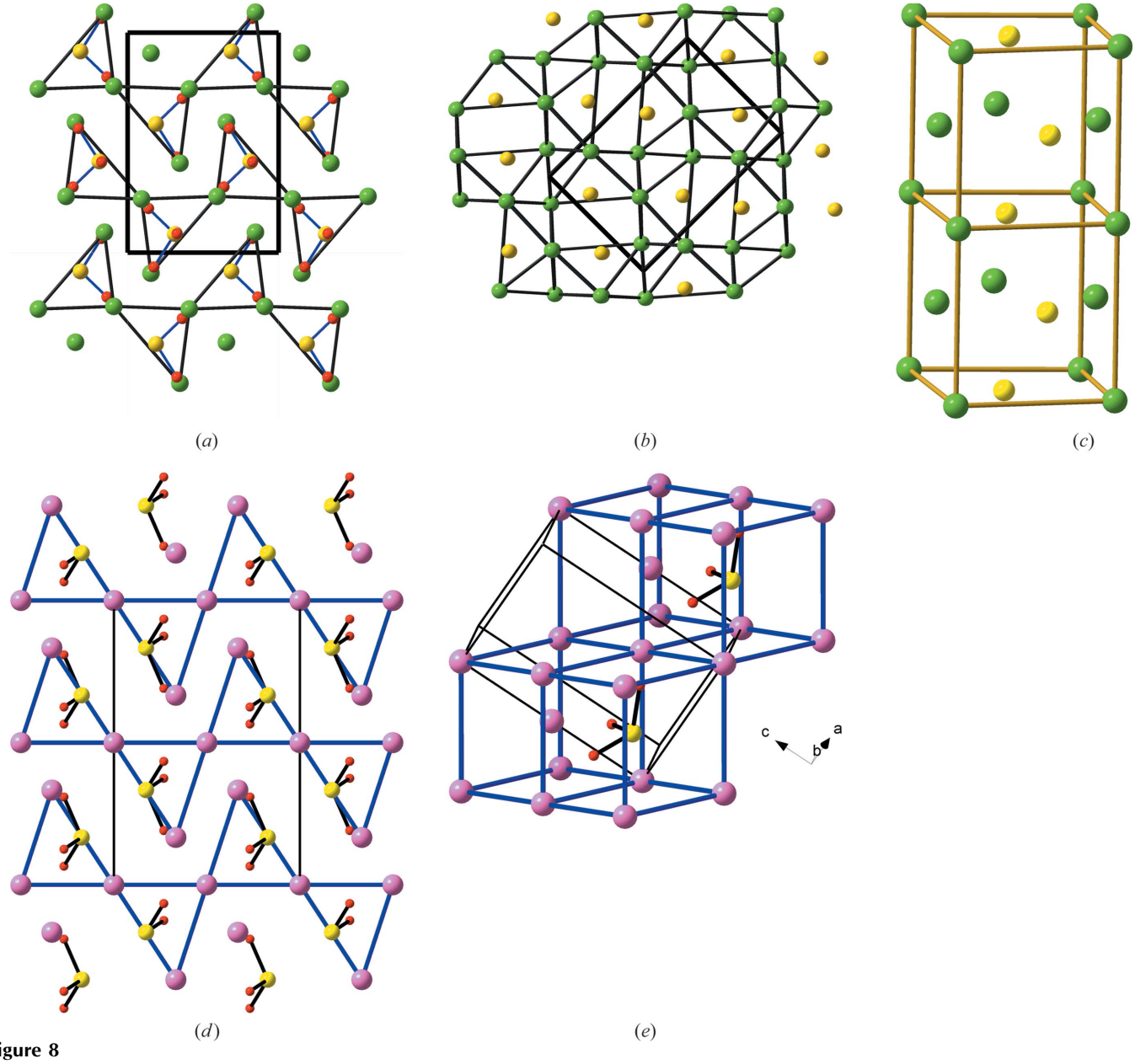

Figure 8
A comparison of the structure of Na_2SeO_3 with that of Na_2SO_3. (*a*) The structure of Na_2SeO_3 viewed along the *a* axis. Very distorted Na_6 trigonal prisms have been drawn to be compared with the corresponding network in Na_2SO_3 as is represented in (*d*); Na: green; Se: yellow; O: red. (*b*) The same array showing the f.c.c. packing formed by the Na and Se atoms altogether. (*c*) Two cubes showing the distorted f.c.c. cells. (*d*) The structure of Na_2SO_3 showing the distorted trigonal Na_6 prisms centred on the SO_3 groups. The Na and S atoms form a Ni_2Al-type structure. (*e*) The alternative description of the structure consisting of slightly distorted Na_8 cubes. Some of them are centred on Na atoms, others by SO_3 groups. Na: violet; S: yellow; O: red.

Table 6
Equivalences found between the structures of M_2S and those of the cation subarrays in their respective M_2SO_x.

These structure types are represented in Fig. 6.

CaF_2	→	Ni_2Al	→	$PbCl_2$	→	Ni_2In	→	$TiSi_2$
Li_2S				High-pressure Li_2S				
Na_2S				High-pressure Na_2S		High-pressure Na_2S		
K_2S						High-pressure K_2S		
Rb_2S				High-pressure Rb_2S		High-pressure Rb_2S		
–		–		Cs_2S		High-pressure Cs_2S		
High-temperature Li_2SO_4		Na_2SO_3 K_2SO_3		K_2SO_4 Cs_2SO_4		High-temperature Na_2SO_4		Room-temperature Na_2SO_4
		High-temperature Cs_2SO_4		High-temperature Na_2SeO_4		High-temperature K_2SO_4		Room-temperature Na_2SeO_4 (thenardite)

(iii) Moreover, in the special case of the sulfoxylates and selenoxylates, this work is additionally important because it will provide a basis for the discussion in the following papers which will be concerned with the possible synthesis of sulfoxylates M_2SO_2 (M = K and Cs) and sodium selenoxylate Na_2SeO_2, as well as a discussion of the relationship between oxidation and pressure in these materials.

As has already been reported (Martínez-Cruz *et al.*, 1994; Vegas & Tranqui, 1996; Vegas, 2000, 2011; Vegas & Mattesini, 2010) the insertion of O atoms into the structure of an alloy (here, the term alloy is applied to the M_2S sulfides) should be equivalent to the application of a physical pressure to the M_2S and M_2Se subarrays from which the oxidized lattices have been formed. This pressure should be proportional to the number of O atoms inserted (Vegas & García-Baonza, 2007; Vegas, 2011) in such a way that the M_2S substructures of the M_2SO_x sulfates would be expected to be related to the high-pressure phases of the respective M_2S sulfides.

Considering the alkali metal sulfides M_2S (M = Li, Na, K, Rb, Cs) together, the observed experimental trend is that their structures undergo the transition path, denoted as **Path 1** in §1, by increasing pressure (Vegas, 2011), and are represented in Fig. 9.

It should be remembered that the relationship between oxidation and pressure – first expressed by Martínez-Cruz *et al.* in 1995, and later confirmed in the high-pressure studies

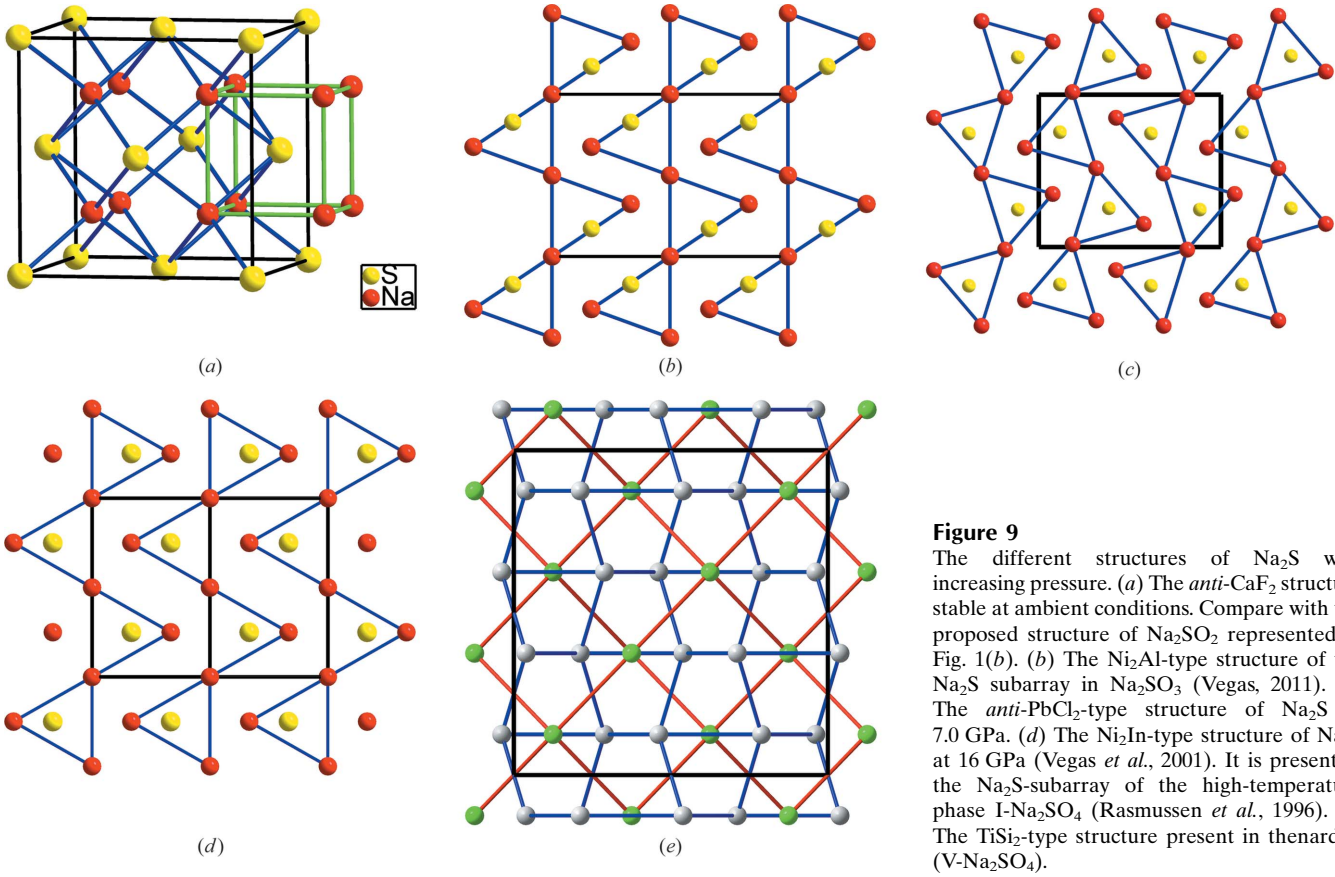

Figure 9
The different structures of Na_2S with increasing pressure. (*a*) The *anti*-CaF_2 structure stable at ambient conditions. Compare with the proposed structure of Na_2SO_2 represented in Fig. 1(*b*). (*b*) The Ni_2Al-type structure of the Na_2S subarray in Na_2SO_3 (Vegas, 2011). (*c*) The *anti*-$PbCl_2$-type structure of Na_2S at 7.0 GPa. (*d*) The Ni_2In-type structure of Na_2S at 16 GPa (Vegas *et al.*, 2001). It is present in the Na_2S-subarray of the high-temperature phase I-Na_2SO_4 (Rasmussen *et al.*, 1996). (*e*) The $TiSi_2$-type structure present in thenardite (V-Na_2SO_4).

carried out on the Li_2S (Grzechnik *et al.*, 2000), Na_2S (Vegas *et al.*, 2001), K_2S (Vegas *et al.*, 2002), Rb_2S (Santamaria-Perez *et al.*, 2011*a*), Cs_2S (Santamaría-Pérez *et al.*, 2011*b*) sulfides – leads to the situation that in the corresponding M_2SO_x (M = Li, Na, K, Rb, Cs) sulfates, the insertion of the O atoms provokes a phase transition in their M_2S substructures. The expected structural change would lead to the situation where in the oxides (sulfates) we should expect to find one (or more) of these high-pressure phases adopted by the M_2S sulfides. That is, insertion of O atoms induces the stabilization of the structures which are found in the high-pressure phases of the alloy (in this case, M_2S). The question as to which of the phases as quoted in path 1 is stabilized in the oxide will depend on the number of O atoms inserted in the sulfide lattice.

Thus, in Table 6 we list the equivalences found between the structures of M_2S and those of the cation subarrays in their respective M_2SO_x. Here, the data given are restricted to sulfides, but should the whole of the chalcogenides be compared, the relationships would become even more evident (Vegas, 2011). Compare with the structures in Fig. 9.

Referring to Table 6 on increasing external pressure on the lattice, the double transition: anti-fluorite (*anti*-CaF_2) → *anti*-$PbCl_2$ → Ni_2In has been observed for Na_2S (Vegas *et al.*, 2001). However, a complete analysis (Vegas, 2011) of the transitions observed in both M_2T and M_2TO_x (T = S, P, Si *etc.*) compounds has also revealed a surprising parallelism between both families of compounds which implies that the complete structural transition path for Na_2S might well be that quoted in the top of Table 6.

The fact that the Ni_2In-type structure is present in the high-temperature (HT) phase of Na_2SO_4, and that the Na_2S subarray is of Ni_2Al-type in Na_2SO_3, indicates that the CaF_2-type is likely to be the most probable structure for this same subarray in the sulfoxylate, Na_2SO_2. The predicted structure is drawn in Fig. 1. The known behaviour of the related Li_2SO_4, K_2SO_4 and K_2SO_3 compounds further supports our predictions. It is perhaps important to emphasize that the evolving structures are either retaining their heavy-atom positions [metal and sulfur] or provoking stabilization of the other high-pressure structures whilst adding in additional O atoms. Comparing Table 6 and Fig. 9 we can see that oxides and alloys undergo the same phase transitions. Three factors influence the structural changes, *i.e.* the O content (x), pressure and temperature.

Thus, the phenakite-related structure of β-Li_2SO_4 becomes anti-fluorite at high temperature. K_2SO_4 *anti*-$PbCl_2$ under ambient conditions, transforms into Ni_2In-type at higher temperatures and the sulfites K_2SO_3 and Na_2SO_3 are both of the Ni_2Al-type (Vegas, 2011; see Fig. 7). Both Na_2SO_4 and Na_2SeO_4 are under ambient conditions of the $TiSi_2$-type but they transform at high temperatures into the Ni_2In- and the *anti*-$PbCl_2$-types, respectively. As discussed above, for the compounds Na_2SO_3 and Na_2SeO_3 the result is as expected, that is, the lower O content corresponds to the production of lower pressure, yielding cation arrays closer to the parent CaF_2-type structure of Na_2S and Na_2Se.

In connection with Vegas' crystallographic studies (Martínez-Cruz *et al.*, 1994; Vegas & Martínez-Cruz, 1995; Santamaria-Perez & Vegas, 2003; Santamaria-Perez *et al.*, 2005; Vegas, 2000, 2011; Vegas & García-Baonza, 2007; Vegas *et al.*, 2009), and from the experimental high-pressure work by Marqués *et al.* (2009), we are anxious to demonstrate the antifluorite structure for the sulfoxylate salts. The thermodynamic and volumetric data discussed in this paper will form the basis of a VBC discussion (AV and HDBJ) of this work and other work (AV) will report the outcome of the practical synthesis planned.

Dr Javier Medrano (CIB, CSIC, Madrid) is thanked for his kind assistance in redrawing Figs. 3, 4 and 5. Professor Jenkins would like to acknowledge the support of the University of Warwick for providing facilities to enable this work to be undertaken. Dr Angel Vegas (Madrid) and Professors Fernando Rey (Valencia) and Francisco Javier Manjón (Valencia) and their colleagues are thanked for arranging and supporting a visit to the Instituto de Tecnología Química Valencia (UPV-CSIC), España by HDBJ. Professor Jenkins thanks his colleagues: Dr Nathaniel W. Alcock, OBE, FSA, for useful comments and Dr Diane Holland for advice on error treatment. One of our reviewers kindly brought to our attention some additional data for which we thank him/her and another reviewer focused our attention on stability of the sulfoxylates with respect to their individual corresponding sulfide and sulfate. AV is thanked for introducing HDBJ to Juan de Cabanilles', *Batalla Imperial de Quinto Tono* as played on the XVIIth Century Echeverría Orguel of Toledo's 'Santa María' Cathedral by Paulino Ortiz.

References

Barin, I. (1993). *Thermochemical Data for Pure Substances*. Weinheim: VCH.
Beck, H. P. & Lederer, G. (1993). *Z. Anorg. Allg. Chem.* **619**, 897–900.
Cordfunke, E. H. P., Ouweltjes, W. & Prins, G. (1987). *J. Chem. Thermodyn.* **19**, 369–375.
Dasent, W. E. (1965). *Non-Existent Compounds: Compounds of Low Stability.* New York: Marcel Dekker, Inc.
Dixon, D. A., Feller, D., Christe, K. O., Wilson, W. W., Vij, A., Vij, V., Jenkins, H. D., Olson, R. M. & Gordon, M. S. (2004). *J. Am. Chem. Soc.* **126**, 834–843.
Finch, A., Fitch, A. N. & Gates, P. N. (1993). *J. Chem. Soc. Chem. Commun.* pp. 957–958.
Finch, A., Gates, P. N., Jenkins, H. D. B. & Thakur, K. P. (1980). *J. Chem. Soc. Chem. Commun.* pp. 579–580.
Foerster, F., Brosche, A. & Norberg-Schultz, C. (1924). *Z. Phys. Chem.* **110**, 435–496.
Glasser, L. & Jenkins, H. D. B. (2011*a*). *Inorg. Chem.* **50**, 8565–8569.
Glasser, L. & Jenkins, H. D. B. (2011*b*). *J. Chem. Eng. Data*, **56**, 874–880.
Grzechnik, A., Vegas, A., Syassen, K., Loa, I., Hanfland, M. & Jansen, M. (2000). *J. Solid State Chem.* **154**, 603–611.
Hao, Ch., Sharrett, S. M. & Sunderlin, L. S. (2007). *Int. J. Mass Spectrom.* **267**, 357–362.
Jenkins, H. D. B. (2008). *Inorg. Chem.* **47**, 8420–8425.
Jenkins, H. D. B. (2009). *Sci. Prog.* **92**, 91–112.
Jenkins, H. D. B. & Glasser, L. (2003). *Inorg. Chem.* **42**, 8702–8708.

Jenkins, H. D. B., Glasser, L., Klapötke, T. M., Crawford, M. J., Bhasin, K. K., Lee, J., Schrobilgen, G. J., Sunderlin, L. S. & Liebman, J. F. (2004). *Inorg. Chem.* **43**, 6238–6248.
Jenkins, H. D. B., Roobottom, H. K., Passmore, J. & Glasser, L. (1999). *Inorg. Chem.* **38**, 3609–3620.
Jenkins, H. D. B., Sharman, L., Finch, A. & Gates, P. N. (1994). *Polyhedron*, **13**, 1481–1482.
Jenkins, H. D. B., Sharman, L., Finch, A. & Gates, P. N. (1996). *Inorg. Chem.* **35**, 6316–6326.
Jenkins, H. D. B., Thakur, K. P., Finch, A. & Gates, P. N. (1982). *Inorg. Chem.* **21**, 423–426.
Jenkins, H. D. B. & Tudela, D. (2003). *J. Chem. Educ.* **80**, 1482–1487.
Kálmán, A. & Cruickshank, D. W. J. (1970). *Acta Cryst.* B**26**, 436.
Karapet'yants, M. Kh. & Karapet'yants, M. L. (1970). *Thermodynamic Constants of Inorganic and Organic Compounds*, translated by J. Schmorak. Ann Arbor, London: Humphrey Science Publishers.
Latimer, W. M. (1961). *Oxidation Potentials*, 2nd ed. Englewood Cliffs, NJ: Prentice Hall.
Lindberg, G., Larsson, A., Råberg, M., Bostrőm, D., Backman, R. & Nordin, A. (2007). *J. Chem. Thermodyn.* **39**, 44–48.
Marqués, M., Ackland, G. J., Lundegaard, L. F., Stinton, G., Nelmes, R. J., McMahon, M. I. & Contreras-García, J. (2009). *Phys. Rev. Lett.* **103**, 115501.
Martínez-Cruz, L. A., Ramos-Gallardo, A. & Vegas, A. (1994). *J. Solid State Chem.* **110**, 397–398.
Mehrotra, B. N., Eysel, W. & Hahn, T. (1977). *Acta Cryst.* B**33**, 305–306.
Meyer, B., Peter, L. & Shaskey-Rosenlund, C. (1979). *Spectrochim. Acta A*, **35**, 345–354.
Muir, A. S. (1993). *Polyhedron*, **10**, 2217–2219.
Nalbandyan, V. & Novikova, A. (2012). *Acta Cryst.* B**68**, 227–239.
O'Hare, P. A. G., Jensen, K. J. & Johnson, G. K. (1986). *J. Chem. Thermodyn.* **18**, 765–786.
Palmer, D. A., Rard, J. A. & Clegg, S. I. (2002). *J. Chem. Thermodyn.* **34**, 63–102.
Ponikvar, M. & Liebman, J. F. (2004). *Struct. Chem.* **15**, 539–542.
Rasmussen, S. E., Jørgensen, J.-E. & Lundtoft, B. (1996). *J. Appl. Cryst.* **29**, 42–47.
Santamaría-Pérez, D. & Vegas, A. (2003). *Acta Cryst.* B**59**, 305–323.
Santamaría-Pérez, D., Vegas, A. & Liebau, F. (2005). *Struct. Bond.* **118**, 121–177.
Santamaria-Perez, D., Vegas, A., Muehle, C. & Jansen, M. (2011*a*). *Acta Cryst.* B**67**, 109–115.
Santamaría-Pérez, D., Vegas, A., Muehle, C. & Jansen, M. (2011*b*). *J. Chem. Phys.* **135**, 054511.
Schmidt, M. & Wirwoll, B. (1960). *Z. Anorg. Allg. Chem.* **303**, 184–189.
Simon, A. & Schmidt, W. (1960). *Z. Elektrochem.* **64**, 737–741.
Toscano, J. P., Deakyne, C. A. & Liebman, J. F. (2003). *Struct. Chem.* **14**, 315–320.
Vegas, A. (2000). *Crystallogr. Rev.* **7**, 189–286.
Vegas, A. (2011). *Struct. Bond.* **128**, 133–198.
Vegas, A. & García-Baonza, V. (2007). *Acta Cryst.* B**63**, 339–345.
Vegas, A., Grzechnik, A., Hanfland, M., Muehle, C. & Jansen, M. (2002). *Solid State Sci.* **4**, 1077–1081.
Vegas, A., Grzechnik, A., Syassen, K., Loa, I., Hanfland, M. & Jansen, M. (2001). *Acta Cryst.* B**57**, 151–156.
Vegas, A. & Jansen, M. (2002). *Acta Cryst.* B**58**, 38–51.
Vegas, A., Martin, R. L. & Bevan, D. J. M. (2009). *Acta Cryst.* B**65**, 11–21.
Vegas, A. & Martínez-Cruz, L. A. (1995). *Z. Kristallogr.* **210**, 581–584.
Vegas, Á. & Mattesini, M. (2010). *Acta Cryst.* B**66**, 338–344.
Vegas, A. & Tranqui, D. (1996). *Acta Cryst.* A**52**, C333.
Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L. & Nuttall, R. L. (1982). *J. Phys. Chem. Ref. Data*, Suppl. 2, p. 11.
Wickleder, M. S. (2002). *Acta Cryst.* E**58**, i103–i104.
Wiench, D. (1975). Diplomarbeit, Universität Gieβen, Germany.